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Exhaust emissions with ethanol or *n*-butanol diesel fuel blends during transient operation: A review

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ABSTRACT

The present work reviews the literature concerning the effects of alcohol/diesel blends on the exhaust emissions of diesel engines operating under transient conditions, i.e., acceleration, load increase, starting and transient/driving cycles. Two very promising alcohols are covered in this survey, namely ethanol and *n*-butanol. The analysis focuses on all regulated exhaust pollutants, i.e., particulate matter (PM), nitrogen oxides (NO_x), carbon monoxide (CO) and unburned hydrocarbons (HC), with results for unregulated emissions, carbon dioxide and combustion noise radiation also included. The main mechanisms of exhaust emissions during transients are identified and discussed, with respect to the fundamental aspects of transient operation and the differing properties of alcohols relative to the reference diesel oil. Based on the published studies up today, summarization of emissions data and cumulative trends are presented, for the purpose of quantifying the alcohol blends benefits or penalties on the regulated emissions during various driving cycles. Particularly for the emitted PM and smoke, a statistically significant correlation with the oxygen content exists (R^2=0.85 and 0.95, respectively). A similar correlation holds true for the heavy-duty, engine-dynamometer data of engine-out CO. Finally, a detailed list is provided that summarizes the main data from all studies published so far.

Contents

Abbreviations: BTEX, Benzene, toluene, ethylbenzene, xylene and 1,3-butadiene; CI, Compression ignition; CVS, Constant volume sampling; DI, Direct injection; DME, Dimethylether; DOC, Diesel oxidation catalyst; DPF, Diesel particulate filter; ECE15, Urban part of the NEDC; ECU, Engine control unit; EGR, Exhaust gas recirculation; EPA, Environmental Protection Agency; ETC, European transient cycle (for heavy-duty engines); EU, European Union; EUDC, Extra urban driving cycle (of the NEDC); F–T, Fischer–Tropsch; FTP, Federal Test Procedure (USA) for heavy-duty engines; FTP75, Federal Test Procedure (USA) for light-duty vehicles; GHG, Greenhouse gas; HWFET, Highway fuel economy test cycle (USA); LHV, Lower heating value; MY, Model year; NEDC, New European driving cycle; nPAHs, nitro polycyclic aromatic hydrocarbons; OECD, Organization for Economic Cooperation and Development; PAHs, Polycyclic aromatic hydrocarbons; PCCI, Premixed-charge compression ignition; PM, Particulate matter; PME, Palm methyl ester; REE, Rapeseed ethyl ester; RME, Rapeseed methyl ester; SME, Soybean methyl ester; UDDS, Urban dynamometer driving schedule (USA) for heavy-duty vehicles; US06, Supplemental federal test procedure (USA) for light-duty vehicles; VGT, Variable geometry turbocharger; *v*/*v*, per volume; w/w, per weight

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1. Introduction

During the last decades, a substantial effort to develop alternative fuel sources, most notably biofuels, has been in progress worldwide, motivated by both economic and environmental issues. Diminishing petroleum reserves and increasing prices, as well as continuously rising concern over energy security, environmental degradation and global warming have been identified as the most influential environmental ones [1].

As regards the financial aspect, the increasing oil prices impose an obvious burden on the trade balances of the non-oil producing countries. In any case, it has been recently argued that if world oil supply should continue to remain generally flat, a possibility exists that oil consumption in OECD countries will continue to decline, as emerging markets consume a greater share of the total oil that is available. If this should be the case, then it is possible that a continuing financial crisis similar to the 2008–2009 recession period might be experienced combined with significant debt defaults [2].

Apart from the economic issues, the extensive use of fossil fuels is responsible for a long-term environmental threat in the form of climatic changes and the slow (but continuous) increase in the average global temperature. The main contributor to the warming of the climate system is the carbon dioxide (CO_2) emitted from various combustion sources. According to the US EPA Inventory of US Greenhouse Gas (GHG) Emissions and Sinks 1990–2009, the transportation sector collectively (including marine and air-transport too) accounted for 27.4% of the total US GHG emissions from end-use fossil fuel combustion in 2009. Passenger cars, light-duty trucks and medium/heavy-duty vehicles alone were responsible for almost 86% of the CO_2 emitted from all transportation sources [3]. Then, it appears that biofuels, possessing the critical merit of being renewable and thus showing an inherent benefit in mitigating CO_2 emissions, seem particularly suitable as viable alternatives to the current situation of the (almost) exclusive use of fossil fuels in automotive and truck applications [1,4–8]. To this aim, the European Parliament passed Directive 2009/28/EC [9] on the promotion of the use of energy from renewable sources, which contains a specific mandate for Member States to include 10% (by energy content) of renewable fuel in the transport sector by 2020. The latter one is expected to be met largely by biofuels. The mandate includes specific sustainability criteria, including a requirement that the fuels meet a 35% GHG saving initially, rising to 60% in 2017, as well as a requirement that biofuels used to meet the target are not produced from land with high carbon stock. In parallel in the US, the Energy Independence and Security Act of 2007 (EISA) increased the original Renewable Fuels Standard (RFS) target of 34 billion liters renewable fuel production in 2008 to 136 billion liters by 2022. Such key mandates are expected to boost the market share of biofuels in the near future. Currently (2009), biofuels account for only 0.6% of the global final energy consumption, in contrast to 81% from fossil fuels and 2.8% from nuclear resources [10].

The term biofuel refers to any fuel that derives from biomass, such as sugars, vegetable oils, animal fats, etc. Biofuels made from agricultural products (oxygenated by nature) reduce the dependence of countries on oil imports, support local agricultural industries and enhance farming incomes [1,4–8]. Moreover, they are way more evenly distributed than fossil or nuclear resources. This fact renders biofuels a very attractive tool in the endeavor towards increased energy security and diversity, which are essential factors for the aforementioned economic stability.

There are numerous biofuels that have been produced and researched so far, e.g., a variety of vegetable oils, different methyl and ethyl esters (biodiesels), bio-dimethylether, bio-hydrogen, bio-alcohols etc. At the moment, biodiesel is considered the primary alternative fuel for compression ignition (CI) engines, since it possesses similar properties to diesel fuel and can also be blended with diesel practically at any proportion, without changes in the existing distribution infrastructure. It is true that bio-alcohols, particularly ethanol and *n*-butanol, were initially considered as fuels for gasoline engines. Nonetheless, they are very promising for CI engines too (blended in smaller proportions with the diesel fuel), since they demonstrate a considerable potential for greenhouse gas emission reduction [1,6,7]. In fact, life-cycle analyses have revealed that typical CO_2 savings from the use of ethanol ranges from 32% (in the case of wheat feedstock) up to 87% (wheat straw feedstock) [9]. It is not surprising then that ethanol production has boomed in the last years with a 17% growth rate during 2010 [10].

It is also well recognized today that one more significant benefit of adding biofuels in the fuel blend is the reduction of the emitted particulate matter (PM) from diesel engines [5–8]. Since the alcohol molecule possesses higher oxygen content compared to biodiesel, the respective potential for PM emission reduction is accordingly higher [6–8]. This is a very promising fact in view of the ever tightening emissions regulations concerning passenger cars and heavy-duty diesel engines.

The diesel engine has for many decades now assumed a leading role in both the medium and medium–large transport sector. Major contributors to this are factors such as its superior fuel efficiency over its spark ignition counterpart, its reliability, as well as its inherent capability to operate turbocharged. Nonetheless, discrepancies in the form of exhaust smokiness and noise radiation delayed its infiltration and wide acceptance in the highly competitive passenger car market. Historically, the majority of the research and published studies on diesel engine operation has focused on the steady-state performance. However, only a very small fraction of a vehicle's operating pattern is true steady-state. As a matter of fact, the greater part of the daily driving schedules of passenger cars, trucks and non-road engines involves transient operation in the form of changing engine speed and/or loading/fueling conditions.

The fundamental aspect of turbocharged transient conditions lies in their operating discrepancies compared with the respective steady-state ones. Whereas during steady-state operation, engine speed and fueling remain essentially constant, under transient conditions both the engine speed and the fuel supply change continuously. Consequently, the available exhaust gas energy varies, affecting the turbocharger shaft torque balance, and hence the boost pressure and the air-supply to the engine cylinders. However, due to various dynamic, thermal and fluid delays,

Nomenclature

p	pressure (bar)
φ	crank angle (deg.)
Φ	fuel–air equivalence ratio

mainly originating in the turbocharger moment of inertia, combustion air-supply is delayed compared with fueling, thus adversely affecting torque build-up and vehicle driveability. What is equally important is that, as a result of this delay in the response between air-supply and fueling, PM and gaseous emissions peak way beyond their acceptable steady-state values [11]. A typical representation is illustrated in Fig. 1 as regards smoke opacity and nitrogen oxides (NO_x) development during an acceleration event of a turbocharged diesel engine. Acknowledging these well established transient emission discrepancies, legislative directives in the EU, the US and Japan, have drawn the attention of manufacturers and researchers to the dynamic operation of diesel engines in the form of transient cycles certification for new engines/vehicles [12,13].

The target of the present work is to review the literature regarding the impacts of alcohol/diesel blends on the exhaust emissions of compression ignition engines, under the very critical transient conditions encountered in the everyday operation of engines and vehicles, i.e., acceleration, load increase, starting and in the collective form of driving cycles. The biofuels that are considered in the present study are:

a) Bio-ethanol (ethanol), and
b) Bio-butanol (*n*-butanol)

which are considered to possess the greatest potential in the alcohol family, based on grounds of production rate, ease of use, sustainability, and PM reduction capability.

The analysis that follows will primarily focus on the two most influential diesel engine pollutants, PM and NO_x, but results for carbon monoxide (CO) and unburned hydrocarbons (HC), as well as for unregulated exhaust emissions, CO_2 and combustion noise

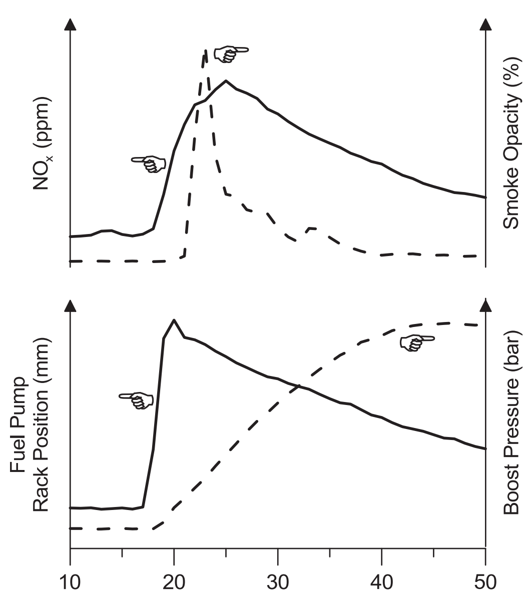


Fig. 1. Qualitative fueling vs. air-supply (boost pressure) response, highlighting the turbocharger lag and its inter-relation with smoke opacity and NO_x emission spikes, typical at the onset of each acceleration or load-increase event.

radiation will also be presented. The usual approach when analyzing alternative fuel impacts on exhaust emissions is by discussing the differing physical and chemical properties of the various blends against those of the reference fuel. Consequently, the composition and properties of the ethanol and *n*-butanol, together with their combustion and emission formation mechanisms, will form the basis for the interpretation of the experimental findings. As of equal importance, emphasis will be placed on the discrepancies encountered during transients too, which may enhance or alleviate the differences observed between the biofuel blends and the neat diesel fuel operation.

2. Fundamental aspects of alcohols chemistry and alcohol/diesel blends combustion

2.1. Ethanol

Alcohols are defined by the presence of a hydroxyl group (–OH) attached to one of the carbon atoms. Ethanol, in particular, (or ethyl alcohol) is a biomass-based renewable fuel (bio-ethanol), which can be produced, relatively easily and with low cost, by alcoholic fermentation of sugar from vegetable materials, such as corn, sugar cane, sugar beets, barley, and from (non-food) agricultural residues such as straw, feedstock and waste woods [6,7,14]. Ethanol is isomeric with dimethylether (DME) and both ethanol and DME can be expressed by the chemical formula C_2H_6O. Although they may have the same chemical formula, the thermodynamic behavior of ethanol differs significantly from that of DME on account of its stronger molecular association via hydrogen bonds.

Because of its high octane number, ethanol is considered primarily a good spark-ignition engine fuel. Nonetheless, it has been considered also a suitable fuel for compression ignition engines, mainly in the form of blends with diesel fuel [1,6,7,15,16], although investigations with pure ethanol (or methanol) have been conducted too [17,18]. For the latter case, cetane improvers and/or glow plugs were implemented combined with an increase in the engine compression ratio to facilitate ignition, particularly during cold starting.

Another successful method for using alcohols in diesel engines is fumigation. In this technique, alcohol is atomized in the engine's intake air either by carburetion or injection. Diesel fuel is directly injected into the cylinder and the combined air–alcohol/diesel mixture is auto-ignited, with diesel fuel consumption being reduced by the energy of the alcohol in the intake air. This procedure, however, requires separate fuel systems for the diesel and ethanol fuel. Additionally, the amount of alcohol used is practically limited by the amount that can be vaporized into the intake air. As a result, this approach seems more feasible as an engine retrofit, where total energy substitution is not the primary objective [7,19]. However, unlike gasoline or diesel fuel, the vapors of ethanol above the liquid fuel in the fuel-tank are usually combustible at ambient temperatures, posing a risk of explosion particularly during refueling.

The use of ethanol as substitute for gasoline gained considerable interest, mostly in the US (corn-based ethanol) and Brazil (sugar cane-based ethanol), following the global fuel crisis in the 1970s, although early applications originate from the 1930s [6,7].

The initial investigations into the use of ethanol in diesel engines, on the other hand, were initiated in South Africa in the 1970s, and continued in Germany and the US during the 1980s. Most of these works related to the use of in-farm equipment (tractors and combines) e.g., [20] and employed an ethanol/diesel fuel blend. The main benefit from the use of ethanol during (steady-state) diesel engine operation is the significant reduction of PM/smoke, due to the high oxygen content of the fuel blend [6,7,21–28]. Carbon monoxide emissions have been reported lower too, but NO_x as well as unburned HC may increase. At the same time, the specific fuel consumption has been reported usually higher owing to the alcohol's lower calorific value, but at a lower percentage compared to the decrease of the calorific value, hence the brake thermal efficiency is (usually) slightly higher [7].

In any case, there are several critical issues to consider with the use of ethanol in the diesel fuel. While anhydrous ethanol is soluble in gasoline, its miscibility in diesel fuel is problematic. This is one of the most important drawbacks since, if unattended, it may cause phase separation between diesel fuel and ethanol, with serious consequences on the engine operation. This is why additives in the form of emulsifiers or co-solvents are usually applied in order to ensure solubility of anhydrous ethanol in the diesel fuel, especially at low temperatures (below 10 °C). Moreover, ethanol possesses lower flash point and lower viscosity than diesel fuel. Ethanol addition in the diesel fuel reduces the lubricity of the blend and creates potential wear problems in fuel pumps, particularly during starting, primarily in rotary and distributor-type pumps but also in modern common-rail systems that employ a fuel-based lubrication. Ethanol, apart from having a lower calorific value than diesel fuel, is also characterized by corrosiveness and a much lower cetane number that reduces the cetane level of the diesel/ethanol blend, thus requiring the use of cetane enhancing additives for improving ignition delay and mitigating cyclic irregularity [6,7,29–32].

In view or the previously mentioned disadvantages, another alternative has gained interest recently, namely simultaneous use of diesel, biodiesel and ethanol (or *n*-butanol). This three-component blend combines the benefits from the two biofuels and also aids in the better solubility of ethanol in the fuel blend using the biodiesel as the co-solvent. Moreover, since biodiesel is characterized by higher viscosity, lubricity, cetane number and flash point relative to ethanol, all the above-mentioned 'obstacles' of using ethanol alone in the diesel blend seem to be, at least partially, overcome [33–35].

2.2. *n-butanol*

A very challenging alcohol competitor for use as fuel in diesel engines is butanol (butyl alcohol). Like ethanol, butanol is a biomass-based renewable fuel that can be produced by alcoholic fermentation of sugar beet, sugar cane, corn, wheat (bio-butanol), although petro-butanol also exists, i.e., butanol produced from fossil fuels. Moreover, in order to increase the production scale and avoid the use of food crops, there is an ongoing research effort aimed at developing the technology to process lignocellulosic biomass (wood, grasses, agricultural wastes, etc) into butanol too. Butanol ($CH_3(CH_2)_3OH$) has a four-carbon structure and is a higher-chain alcohol than ethanol, as the carbon atoms can either form a straight chain or a branched structure, thus resulting in different properties. Consequently, it exists as different isomers depending on the location of the hydroxyl group (–OH) and carbon chain structure, with butanol production from biomass tending to yield mainly straight chain molecules. 1-butanol, better known as *n*-butanol (normal butanol), has a straight-chain structure with the hydroxyl group (–OH) at the terminal carbon [8].

n-Butanol is of particular interest as a renewable biofuel as it is less hydrophilic, and possesses higher energy content, higher cetane number, higher viscosity, lower vapor pressure, higher flash point and higher miscibility than ethanol, making it more preferable than ethanol for blending with diesel fuel. Therefore, the problems associated with ethanol mentioned in the previous sub-section are solved to a considerable extent when using *n*-butanol, which is also less corrosive. However at the moment, its production rate by ABE (acetone butanol ethanol) fermentation is much lower than that of the yeast ethanol fermentation process, a fact explaining the much more vigorous research on ethanol compared with *n*-butanol during the last decades, particularly after the petroleum crisis in the 1970s [8].

The literature concerning the use of *n*-butanol/diesel fuel blends in diesel engines and its effects on their steady-state performance and (exhaust) emissions is limited, but with a steadily rising trend. An early study by Yoshimoto et al. [34] dealt with the performance and exhaust emission characteristics of a diesel engine fueled with vegetable oils blended with oxygenated organic compounds, including *n*-butanol. Rakopoulos et al. published results from an experimental investigation on a high-speed DI diesel engine [36], and on a medium-duty diesel engine [37] during steady-state conditions. These studies revealed the beneficial effects of using various blends of *n*-butanol with diesel fuel on smoke and CO emissions at various loads, however at the expense of higher NO_x and HC emissions. Again, it is the high oxygen content of *n*-butanol that leads to enhanced in-cylinder soot oxidation, which is responsible for the decrease in smoke emissions. Similar results were reached by Yao et al. [38], Lujaji et al. [39] (croton oil was included in the fuel blend) and Dogan [40], all referring to steady-state experimentation. As is also the case with biodiesel and ethanol blends, engine operation with *n*-butanol/diesel fuel has been found to have slightly higher specific fuel consumption as well as a slight increase in brake thermal efficiency.

2.3. *Comparison of physical and chemical properties*

Table 1 summarizes the most important physical and chemical properties of the two alcohols considered in this review against those of the reference diesel fuel. From the data provided in Table 1 it can be concluded that the two alcohols, with respect to the diesel fuel, contain/have:

1. 21–35 wt% oxygen that leads to proportionally lower energy density. Thus, more fuel needs to be injected in order to achieve the same engine power output. Further, the inbound oxygen reduces the fuel–air equivalence ratio and so lowers the exhaust gas temperatures.
2. No aromatic or poly-aromatic hydrocarbons.
3. Zero natural sulfur content (considered a soot precursor). However, this advantage seems to fade away gradually, owing to the continuous desulfurization of the petroleum diesel fuel.
4. Much lower cetane number (CN) (and higher octane number, accordingly). CN represents the ignitability of the fuel, with higher CN leading to shorter ignition delay. The increase in the premixed-phase of combustion originating in the longer ignition delay period of the alcohol-blends results also in a proportionately higher amount of fuel burned under constant volume conditions, which entails higher cycle efficiency but also elevated combustion noise radiation. The ignitability issues associated with the use of alcohols in diesel engines are more prominent during cold starting.
5. Lower heating value owing to the oxygen content (greater mass needs to be injected in order to achieve the same engine power output).

Table 1
Comparison of key physical and chemical properties between ethanol, *n*-butanol and low-sulfur automotive diesel fuel [6–8,30].

	Ethanol C_2H_5OH	*n*-Butanol C_4H_9OH	Low-sulfur automotive diesel fuel
Density/15 °C (kg/m^3)	789	810	820–850
Kinematic viscosity/40 °C (cSt)	1.20	2.5	2–3.5
Cetane number	5–8	17 [30] 25 [8]	~50
Octane number	108	96	20–30
Lower heating value (kJ/kg)	26,800	33,000	~43,000
Molecular weight (kg/kmol)	46	74	170
Carbon content *C* (% weight)	52.2	64.8	84–87
Hydrogen content *H* (% weight)	13.1	13.5	16–13
Oxygen content *O* (% weight)	34.7	21.6	0
C/H atom ratio	0.33	0.40	0.45
Sulfur content (ppm)	0	0	< 50 (< 10 for ultra low-sulfur diesel fuel)
Stoichiometric air–fuel ratio	9	11.2	~15
Latent heat of evaporation (kJ/kg)	900	585	265
Boiling temperature (°C)	78	118	180–360
Lubricity (μm)	950	590	310
Flammability limits (% vol.)	3.3–19	1.4–11.2	1.5–7.6
Bulk modulus of elasticity (bar)	13,200	15,000	16,000
Flash point (°C)	13	35	50–90

6. Lower density, so that volumetrically-operating fuel pumps inject smaller mass of alcohol than conventional diesel fuel.
7. Lower flash point, which is a measure of the temperature to which a fuel must be heated such that the mixture of vapor and air above the fuel can be ignited. Ethanol is way less safe than diesel fuel in that respect.
8. Smaller carbon to hydrogen atom ratio (C:H), particularly for ethanol. This affects (reduces) the adiabatic flame temperature.
9. Higher heat of vaporization, particularly for ethanol. Thus, larger amount of heat is needed to evaporate the liquid alcohol, which eventually leads to smaller amount of heat remaining for the increase of the gas temperature.

In general, the higher the number of carbon atoms in the alcohol molecule, the lower its oxygen content and hence its potential for soot reduction (as will be discussed later in the text), but also the higher its cetane number, LHV, density, stoichiometric air–fuel ratio and viscosity, thus rendering it more compatible with diesel fuel [30]. Consequently, based on the physical and chemical properties alone, as these are documented in Table 1, *n*-butanol seems more appropriate than ethanol to be used in a diesel engine. In support to this argument, Lapuerta et al. [30] analyzing various physical and chemical properties of the first five alcohols concluded that *n*-butanol can be blended with diesel fuel practically at any rate without concerns over stability (above 0 °C), viscosity or cold-flow properties, whereas blends up to 35% should only be applied based on potential lubricity problems. On the other hand, various blending limitations are valid for ethanol apart from lubricity.

3. Historical overview

Table A in the Appendix provides a list of the published papers in International Journals and well established conferences, as well as of the reports from renowned research centers that all deal with exhaust emissions during (truly) transient conditions, when the engine runs on ethanol or *n*-butanol/diesel fuel blends [41–64] (hence, no steady-state cycles, such as the ECE R49, are included). The few studies that investigated pure alcohol impacts are not included, since engine modifications are usually required in this case (increase in the compression ratio, glow plugs) and cetane improvers, with all these facts rendering unfeasible a direct comparison with the reference engine operation. On the other hand, the few works that applied a small percentage of biodiesel in the ethanol/diesel fuel blend are included [41,56,58,60,61]. Table A provides information on the experimental procedure of each work, with details about the engine studied (application, model year (MY) or emission level), the transient schedules examined, the alcohol blends tested, and the exhaust pollutants investigated. All the investigations deal with four-stroke passenger cars and medium/heavy-duty or non-road engines/vehicles. The first transient results appeared in the mid-nineties, and it seems that the research has intensified in the last few years, as is also illustrated in the bar-chart diagram of Fig. 2. Ethanol/diesel blends account for more than 70% of the studies so far, as depicted in the upper-left pie diagram in Fig. 2. The impact of alcohol blends on engine emissions during various legislative transient/driving cycles constitutes the most prolific segment of the research (upper-right pie diagram in Fig. 2), but results have also been presented for the more fundamental cases of discrete transient schedules [49,55,57,62,64], where instantaneous emission measurements were accomplished using fast-response emission analyzers.

4. Emission effects of alcohol/diesel fuel blends during transient operation

4.1. Exhaust emissions

As an opening argument for the exhaust emissions discussion that follows, it can be stated that irrespective of the biofuel tested, spray properties may be altered with respect to normal diesel operation owing to differences in the physical and chemical properties such as molecular structure, cetane number, latent heat of vaporization, viscosity, surface tension, bulk modulus of elasticity, and boiling point. All these, in turn, affect the injection timing, the ignition delay, as well as the balance between premixed and diffusion combustion, shifting the emission pattern to lower or higher emission values depending on other specific conditions (blending percentage, injection system and engine technology in general, transient schedule, exhaust gas after-treatment).

4.1.1. Particulate matter and smoke

Diesel particulates consist mainly of combustion generated carbonaceous material (soot) on which some organic (arisen mainly from unburned fuel and lubricating oil) or inorganic compounds have been absorbed. Particulate material is distributed over a wide size range,

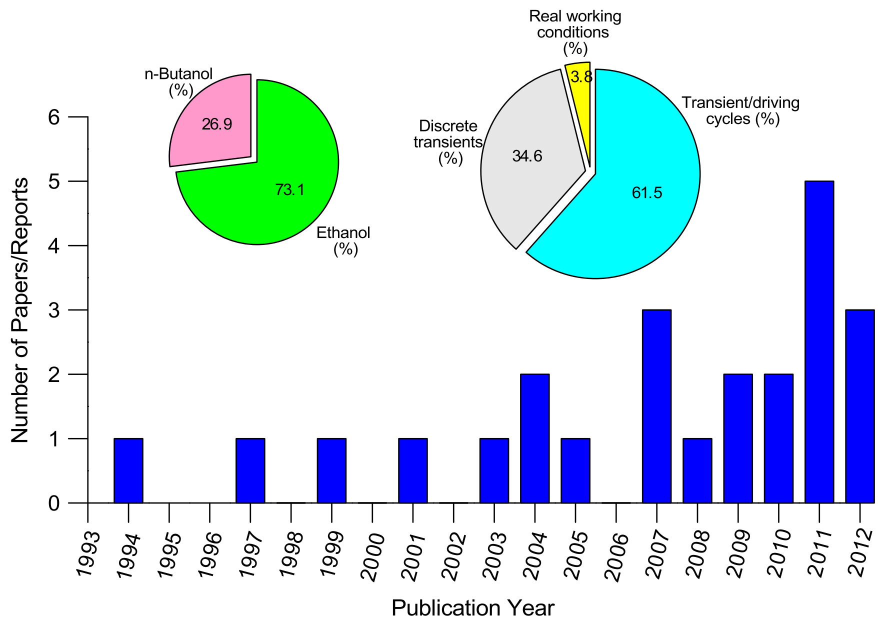


Fig. 2. Quantification of published papers/reports on transient diesel engine emissions with ethanol or *n*-butanol/diesel blends in a chronological order (bar chart) up to 2012, based on the alcohol used (upper left), or the transient schedule tested (upper right).

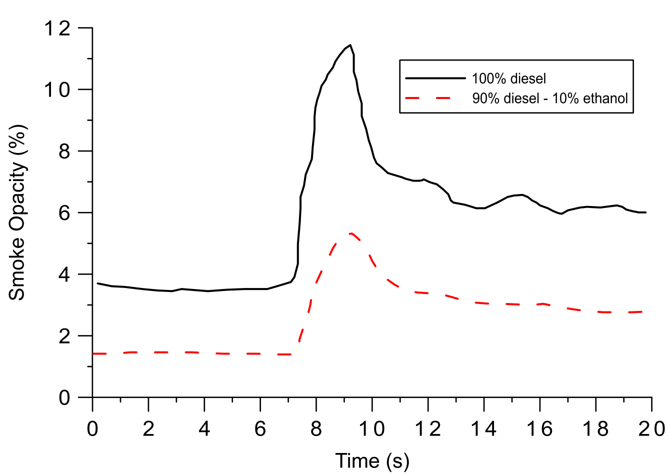


Fig. 3. Smoke opacity development during a 26–90 Nm load increase transient event at 1661 rpm for neat diesel and E10 blend (experimental results adapted from Armas et al. [49]).

typically from 20 nm to 10 μm, thus being respirable. PM is often separated into a soluble organic fraction (SOF) and an insoluble or dry fraction, which is often used as an estimation of soot. Soot is formed from unburned fuel that nucleates from the vapor phase to a solid phase in fuel-rich regions at elevated temperatures [65].

4.1.1.1. Ethanol. As mentioned earlier, oxygenated fuels, and alcohols in particular, have been found capable of (substantially) decreasing particulate matter or smoke during steady-state operation. In general, similar results have been reported during transient conditions too, for both passenger cars and heavy-duty or non-road diesel engines.

A comprehensive investigation into ethanol/diesel fuel blend effects during transients was conducted by Armas et al. [49], who studied discrete transient schedules (cold starting and load increase) of a passenger car engine running on E10 (i.e., 10% ethanol −90% diesel fuel) fuel blend without a stabilizing agent. A typical result from their research is reproduced in Fig. 3, which illustrates smoke opacity[1] development during a load increase at constant speed. As is evident, the ethanol/diesel blend was proven successful in reducing both the peak and the final smoke opacity values throughout the transient event (notice that the initial level was lower for E10, which influenced accordingly the whole transient pattern). Since the inlet air-flows were measured for each fuel to behave similarly during the transient test, it was concluded that the reduced opacity values of E10 can be primarily attributed to the higher oxygen content of ethanol, and also to its lack of sulfur and aromatics that are prone to create soot precursors. Greater reductions in smoke opacity should be expected for higher load increases or sharper accelerations, particularly when these commence from low engine speeds, where the turbocharger lag discrepancies are more prominent [11]. The same applies if higher ethanol percentages are added in the fuel blend, as revealed the results reached by Ahmed [44] (or Spreen [43], who issued the originating report) during the FTP transient cycle of a heavy-duty diesel engine, and by Merritt et al. [48] during the FTP smoke test for three non-road engines. From the latter study, a representative set of results are reproduced in Fig. 4, which demonstrate the superiority of ethanol/diesel blends over mineral oil in substantially reducing the emitted smoke. In support to the previous findings, Table 2 summarizes the results from all ethanol/diesel fuel studies on PM and the other regulated pollutants, which will be discussed later in the text.

Ethanol addition in the fuel blend has been reported beneficial during hot starting too [64], whereas during cold starting the available results are contradicting. In contrast to biodiesel that exhibits worse PM behavior than mineral diesel during cold starting, ethanol addition in the fuel blend was found by Armas et al. [49] to lead to much lower peak in smoke opacity, of the order of 57%, at 18 °C ambient temperature relative to the neat diesel operation. The reduction was attributed to the lower viscosity and higher volatility of ethanol with respect to petroleum diesel, both of which

[1] Although smoke opacity is not among the regulated emissions, it is used by the researchers of discrete transient schedules as a surrogate for the legislated particulate matter, which is more difficult to measure instantaneously in an accurate manner.

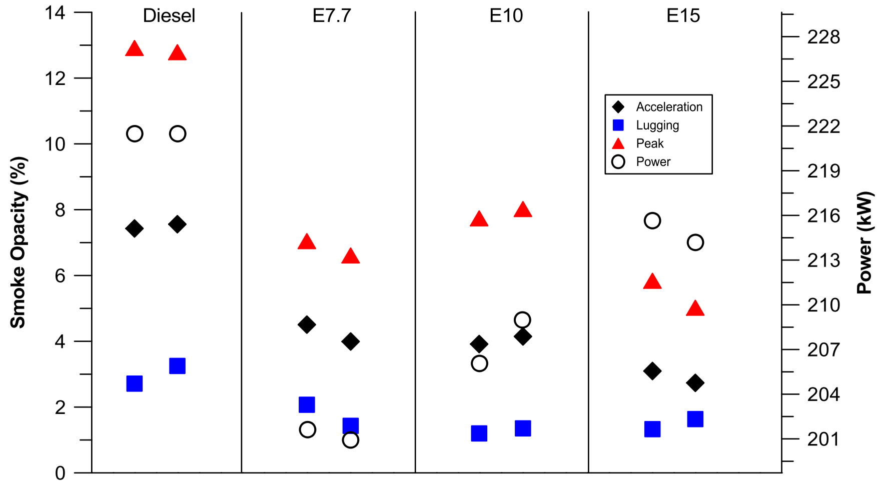


Fig. 4. Cumulative smoke opacity and power results for a 8.1 L non-road engine running on three different ethanol/diesel blends during two runs of the FTP smoke test (adapted from Merritt et al. [48]).

favor the, influential during cold starting, spray atomization and fuel vaporization processes. In a later study, however, of the same research group [64], an opposite trend was reported, with substantial smoke opacity increases experienced during a similar cold starting event, when again 10% *v*/*v* ethanol (or 16% *v*/*v* *n*-butanol) was added in the fuel blend. A possible explanation provided was the fact that during cold starting the opacity detected was not only soot but rather contained high concentrations of hydrocarbons too.

In any case, it should be pointed out that the cold starting procedure was more difficult when the engine was running on ethanol than neat diesel fuel [42,49,66], experiencing cranking for several seconds before firing. This is not unexpected since the former blend has lower cetane number and, again, these starting difficulties are expected to deteriorate with higher blend percentages or lower temperatures.

4.1.1.2. n-Butanol. In parallel to the ethanol studies, Kozak [59] reported results from a 10% *n*-butanol −90% diesel (Bu10) fuel blend during the European passenger car NEDC. The blend was found capable of reducing PM emissions of the order of 21% (see also Table 3 for a detailed list of the emitted exhaust differences from *n*-butanol compared with diesel from all pertinent transient studies) with respect to the reference operation while, interestingly, maintaining the amount of emitted NO_x and CO_2 (g/km), however at the expense of increasing CO and HC emissions.

A more fundamental investigation into the effects of *n*-butanol on diesel engine emissions has been carried out by Rakopoulos et al. regarding discrete transient schedules, experimenting with *n*-butanol/diesel blends during acceleration [55] and hot starting [57] of a turbocharged diesel engine. These investigators concluded that during all accelerations tested, the *n*-butanol/diesel fuel blend emitted lower smoke than the respective neat diesel fuel operation but with higher amounts of NO (in ppm). The investigation included also a biodiesel/diesel fuel blend, which provided basis for an interesting and unique comparison between the two biofuels impacts. Fig. 5 is a typical example from the work reported in Ref. [55]. It illustrates the response of a six-cylinder, medium-duty, turbocharged, DI diesel engine during a medium to high speed acceleration, when running on neat diesel fuel, a blend of 25% *n*-butanol/75% diesel fuel (Bu25), and a blend comprising of 30% (sunflower–cottonseed) biodiesel with 70% diesel (B30). As was the case with the load increase shown in Fig. 3, the measurements were accomplished applying high-response NO and smoke opacity analyzers suitable for fast transient experimentation.

Both biofuel blends demonstrated in Fig. 5 were found to improve (decrease) the engine smoke emission during a demanding acceleration, with a follow on improvement observed also at the final steady-state conditions. However, the reduction in smoke emission was (much) more prominent for the *n*-butanol than the biodiesel blend (as was also its oxygen content). Although fuel injection and spray development differed slightly from the case of neat diesel fuel, it was argued that this behavior originated in the fact that the engine ran overall 'leaner' with respect to the neat diesel fuel case. This holds true because the trapped relative air–fuel ratio remained essentially the same, with the combustion being assisted by the presence of the fuel-bound oxygen of the biodiesel or *n*-butanol in locally crucial rich zones, which seemed to have the dominant influence. In fact, it was the always higher oxygen mass percentage of the *n*-butanol blend relative to the biodiesel one that resulted to its superior smoke behavior. As a result, whereas the peak opacity value was lowered by 'only' 13% for the biodiesel blend, for the (higher-oxygen content) *n*-butanol blend the decrease reached an impressive value of 50% relative to the neat diesel fuel operation.

Further results are documented in Fig. 6 for hot starting this time. Here, the effect of each biofuel on the smoke emissions was found contradicting, viz. the biodiesel blend increased both the peak soot value and the unacceptable smoky period, whereas its *n*-butanol counterpart (confirmed also by the results of Armas et al. [64]) substantially decreased both of them, compared with the neat diesel fuel case; the relative differences were of the order of +40% and −69%, respectively, in the maximum opacity value. Moreover, opacity exceeded the 10% value for 10, 14, and just 3 engine cycles (or 1.9, 2.5, and 0.5 s), respectively, for the neat diesel fuel, the biodiesel and the normal butanol blend cases [57]. For the diesel/*n*-butanol blend, the improvement in smoke emissions was again attributed to the engine running overall 'leaner', since combustion was assisted by the presence of the (now higher) fuel-bound oxygen of the *n*-butanol in the locally rich zones, which seemed to have the dominant influence. During transients of turbocharged diesel engines, this extra oxygen is available inside the cylinder at the point and time where a significant deficiency of air exists from the compressor (during turbocharger lag), and so, indeed, it proved extremely critical for the emission development demonstrated in Fig. 6. Further, as was also the case with ethanol, the lower viscosity of *n*-butanol and its higher volatility compared with biodiesel (and diesel fuel) are also expected to limit the comparative soot production. Perhaps not unsurprisingly, the 'cleaner' operation of the engine

Table 2
Summarization of emission changes from ethanol/diesel combustion relative to reference diesel fuel during transient schedules.

Research group	Ethanol (%)	Transient Schedule	Sulfur content of reference fuel (ppm)	PM/Smoke (%)	NO_x (%)	CO (%)	HC (%)	CO_2 (%)
Peterson, Reece [41][a]	10	Arterial transient cycle	360	20.7	−2.9	58.1	54.8	0.4
McCormick et al. [42]	6.5	Hot FTP	290	−36.9	1.7	−14.9	56.4	–
Ahmed [44]	10	Hot FTP	n/a	−27	−4	−20	~	–
Ahmed [44]	15	Hot FTP		−41	−5	−27	~	–
Corkwell et al. [45]	10	Hot FTP75 (bag 3)	< 10	−16	20	38	56	–
Corkwell et al. [45]	10	Hot US06		−17	19	20	12	–
Frank et al. [46][b]	7	Hot FTP (engine-out)	450	~	−1.8	~	↑↑	2.2
Frank et al. [46][b]	7	Hot FTP (post-DOC)	450	−31	−3.7	32	↑↑	1.6
Fanick [47]	7.7	FTP	500	−7.1	−5.3	−6.3	40	–
Merritt et al. [48]	7.7	FTP smoke test	400	−43/−40/−47 −28/−11/−26 −51/−37/−46	–	–	–	–
Merritt et al. [48]	10	FTP smoke test	400	−45/−53/−39 −36/−30/−33 −56/−20/−53	–	–	–	–
Merritt et al. [48]	15	FTP smoke test	400	−60/−50/−57 −55/−29/−58 −57/−14/−57	–	–	–	–
Armas et al. [49]	10	Cold starting (18 °C)	260	−53.7 (peak)	−13.6 (peak)	–	–	–
Armas et al. [49]	10	Medium-speed load increase		−54.4 (peak)	5.1 (peak)	–	–	–
Armas et al. [49]	10	High-speed load increase		−38.2 (peak)	−4.1 (peak)	–	–	–
Armas et al. [49]	10	Medium-speed load increase from motoring		−57 (peak)	36.4 (peak)	–	–	–
Armas et al. [53]	7.7	Real working conditions	34	−(24÷27)	−(8÷20)	–	–	–
Löfvenberg [54]	10	ETC (engine out)	< 10	−16.2	1.2	−1.7	16.1	3.5
Löfvenberg [54]	10	ETC (post-DOC/DPF)	< 10	−29.4	−2.3	100	↑↑	−3.6
Löfvenberg [54][c]	10	ETC (engine out)	< 10	−13.9	~	3.4	−17.5	4.8
Löfvenberg [54][c]	10	ETC (post-DOC/DPF)	< 10	−34.4	~	~	100	−8.6
Cheenkachorn [56][d]	5	Bangkok cycle (average)	n/a	−39	5.9	−31.9	−6.8	−1
Randazzo, Sodre [58][e]	5	NEDC	90	52.8	−8.2	61.2	102	
Magand et al. [60][f]	20	NEDC	n/a (< 10?)	−50	60	↑↑	108[g]	−1.8
Magand et al. [60][f]	20	NEDC (optimized)	n/a (< 10?)	−50	−21.9	↑↑	3.5[g]	~
Hulwan and Joshi [61][h]	20	Free acceleration	n/a	−14.5	–	–	–	–
Hulwan and Joshi [61][i]	30	Free acceleration	n/a	↑↑	–	–	–	–
Armas et al. [64]	10	Cold starting (17 °C)	n/a	↑↑ (mean)				
Armas et al. [64]	10	Hot starting	n/a	−18% (mean)				

~: Practically unchanged.
↑↑: Considerable increase (greater than 100%).
–: No measurement available.
n/a: Not available.
Smoke measurements: [48], [49], [53], [61], [64].
For Merritt et al. [48], the reported values correspond to acceleration/lugging/peak for a 8.1 L (1st line – see also Fig. 4), a 6.8 L (2nd line) and a 12.5 L engine (3rd line).
[a] E10/REE10/D80, comparison with neat diesel fuel.
[b] average from two tests, one with diesel fuel No. 1 and one with diesel fuel No. 2.
[c] E10/RME5/D85, comparison with RME5/D95.
[d] E5/PME11/D84, comparison with neat diesel fuel.
[e] E5/SME20/D75, comparison with SME20/D80.
[f] E20/F-T/RME/isohexane (9.5% total oxygen content per weight), comparison with neat diesel fuel.
[g] NO_x+HC.
[h] E20/B10/D70, comparison with neat diesel fuel.
[i] E30/B20/D50, comparison with neat diesel fuel.

with the addition of *n*-butanol reported in [57,64] during warm/hot starting, led also to an increase in the number of emitted nanoparticles [64].

The arguments raised previously for discrete transient schedules can be further enhanced with an instructive comparison of smoke emissions between neat diesel fuel and a Bu10 blend reproduced in Fig. 7. The latter illustrates instantaneous smoke emissions during a transient cycle, namely for the 1180s of the European, passenger car NEDC [59]. Again, the *n*-butanol blend was capable of maintaining the absolute smoke emission to lower levels overall (incl. the cold starting phase), particularly at the onset of each acceleration event (cf. Fig. 5) where the turbocharger lag effects are more pronounced, owing to the instantaneous sharp deficiency in the supplied air from the turbocharger compressor.

As was also the case with ethanol blends, a rough engine operation was noticed in [52], during the butanol/diesel cold-started runs, particularly for the high blending ratio (40% *v*/*v*), accompanied by reduced fuel economy that was attributed to increased misfire. Again, advanced injection techniques, with one pilot and one main injection, might prove beneficial in this regard.

Further, as regards the soluble organic fraction (SOF) of the PM, currently there are no studies available that quantify it during transients for either n-butanol or ethanol blends. Merritt et al. [48] Further, reported a clear increasing trend with increasing ethanol in the fuel blend during steady-state conditions (ISO 8178C1–9 mode test). Similar trends hold true for biodiesel blended fuels e.g.,[67].

4.1.1.3. Summarization of main causes. Summarizing, the main causes for the (beneficial) effects on PM/smoke emissions when adding ethanol or *n*-butanol in the fuel blend are:

Table 3
Summarization of emission changes from *n*-butanol/diesel combustion relative to reference diesel fuel during transient schedules.

Research Group	*n*-Butanol (%)	Transient Schedule	Sulfur content of reference fuel (ppm)	PM/Smoke (%)	NO_x (%)	CO (%)	HC (%)	CO_2 (%)
Miers et al. [52]	20	Hot UDDS		–	~	53	↑↑	~
Miers et al. [52]	40	Hot UDDS		–	−7.1	↑↑	↑↑	6
Miers et al. [52]	20	Cold UDDS	11.6	–	−8	–	–	–
Miers et al. [52]	40	Cold UDDS		–	−15	76	↑↑	8
Miers et al. [52]	20	HWFET		–	12.5	~	~	~
Miers et al. [52]	40	HWFET		–	25	~	~	~
Rakopoulos et al. [55]	25	Low-load, low-high speed acceleration		−73.0 (peak) −57.9 (cum.)	+28.7 (peak)[a] +12.9 (cum.)[a]	–	–	–
Rakopoulos et al. [55]	25	Low-load, medium-high speed acceleration	38	−50.4 (peak) −38.9 (cum.)	+33.8 (peak)[a] +36.2 (cum.)[a]	–	–	–
Rakopoulos et al. [55]	25	Medium-high load, low-high speed acceleration		−55.5 (peak) −56.6 (cum.)	+34.6 (peak)[a] +21.9 (cum.)[a]	–	–	–
Rakopoulos et al. [57]	25	Hot starting	38	−69 (peak)	+51 (peak)[a]	–	–	–
Kozak [59]	10	NEDC		−21	−1	↑↑	↑↑	~
Kozak [59]	10	ECE15 (cold)	8.8	−14	−8.5	↑↑	↑↑	~
Kozak [59]	10	EUDC		−25	7	–	45	~
Armas et al. [64]	16	Cold starting (17 °C)	n/a	↑↑ (mean)				
Armas et al. [64]	16	Hot starting	n/a	−20.5% (mean)				

~: Practically unchanged.
↑↑: Considerable increase (greater than 100%).
–: No measurement available.
Smoke measurements: [55], [57], [64].
n/a: Not available.
cum.: Cumulative.
[a] nitric oxide (NO) measurements.

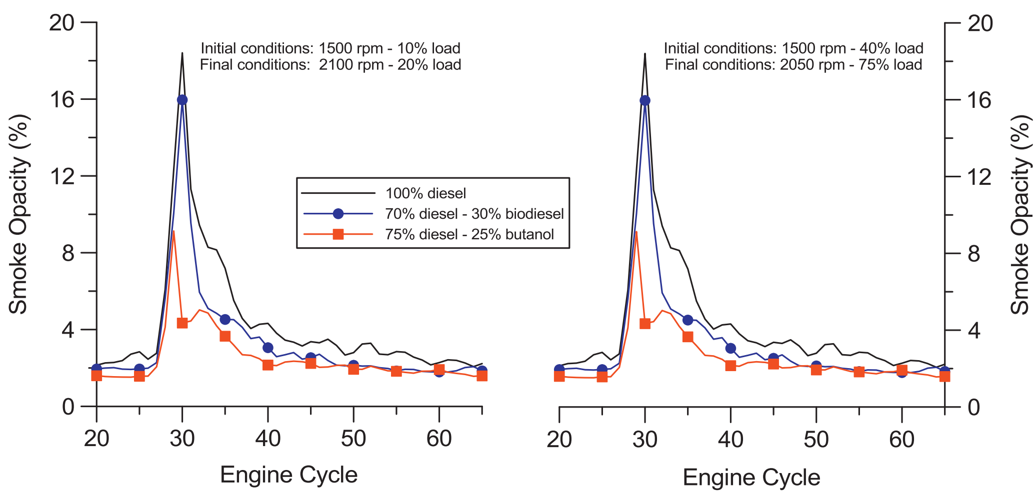


Fig. 5. Development of smoke opacity response during two accelerations of a medium-duty turbocharged diesel engine for neat diesel, Bu25 and B30 fuel blends [55].

- Increased oxygen concentration in the alcohol/diesel blend, which aids the soot oxidation process. Soot formation, caused by high temperature decomposition, mainly takes place in the fuel-rich zone at high temperatures and pressures, specifically within the core region of each fuel spray. If the fuel is partially oxygenated, as is the case with alcohols (and biofuels in general), it possesses the ability to reduce locally fuel-rich regions and limit soot formation, thus reducing PM emissions and smoke opacity. Further, the formation of soot is strongly dependent on engine load, with higher loads (e.g., cruising portions of the driving cycle) promoting higher temperatures, longer duration of diffusion combustion (where particles are mostly formed), and lower overall oxygen availability (air–fuel equivalence ratio). The locally very high values of fuel–air ratio experienced during turbocharger lag at the onset of each acceleration and load increase, enhance the above mechanism that is more pronounced the higher the engine rating, i.e., the higher the full-fueling to no-fueling difference. The excess oxygen inherent in the alcohol molecule aids in maintaining these fuel–air equivalence ratio discrepancies during turbocharger lag (where soot is primarily produced [11]) milder relative to the neat diesel transient operation.
- Alcohols are characterized by lower stoichiometric air–fuel ratio (less air is needed to achieve stoichiometry and consequently complete combustion), which reduces the possibility of existence of fuel-rich regions in the non-uniform fuel–air mixture.
- Absence of aromatic (primarily) and sulfur (secondarily, owing to the continuously decreasing sulfur content in the conventional diesel fuel) compounds that are generally considered to act as soot precursors.
- Further, and in order to account for the lower heating value of alcohols, fuel consumption must increase for the same demanded engine torque. Hence, the ECU strategy dictates an earlier start of injection and, more importantly, a decrease in the exhaust gas recirculation (EGR) rate, both of which result in elevated temperatures inside the cylinder that promote soot oxidation.

- Most of the previous points are, in general, valid for every oxygenated fuel. However, as will be discussed later in the text (Section 4.1.5), combustion of different biofuels results in different PM benefits over the reference diesel fuel operation, even if the oxygen content in the fuel blend is the same. This clearly implies that there are other contributing factors, apart from the oxygen content, that define the PM emission profile. Shudo et al. [68] found that when blending ethanol to palm methyl ester, the flame region with high luminosity and high temperature shrank. This suggests that the ethanol blending increased premixed combustion and reduced the region with high local fuel–air equivalence ratio, which leads to the soot formation. Likewise, Botero et al. [69] reported that the addition of ethanol to diesel fuel delayed the onset of the yellow luminosity of the flame, because of its volatility and thereby preferential gasification. This indicates a corresponding reduction in soot formation during the early stage of burning, when the flame size and thereby soot content are large, which was not evident during their experiments with biodiesel. The fact that alcohols possess lower CN and higher heat of evaporation means that the ignition delay period increases when an alcohol is added into the fuel blend, increasing accordingly the amount of fuel burned during the premixed phase of combustion. Consequently, a reduction in the diffusion phase is experienced where the majority of soot is normally produced.

4.1.2. Nitrogen oxides

Nitrogen oxides together with particulate matter are the most critical pollutants produced by diesel engines. Nitrogen oxides consist mostly of nitric oxide (or nitrogen monoxide) NO and nitrogen dioxide NO_2, and are referred to collectively as NO_x. Nitrogen oxides production is strongly dependent on temperature (primary dependence), local concentration of oxygen and duration of combustion; other notable factors are injection timing and fuel properties. Nitrogen oxides are highly active ozone precursors playing an important role in the smog chemistry. Unlike soot that experiences both in-cylinder production and destruction, during expansion the NO_x concentration 'freezes', hence all the produced amount of NO_x is transferred into the exhaust.

The most successful method of reducing nitrogen oxides emissions is by lowering the peak cylinder temperature through retarded injection timing (this may, however, affect engine efficiency) or, more successfully, applying exhaust gas recirculation. The latter method has been rendered very popular in recent years as an efficient means for reducing the emitted NO_x from both spark and compression ignition engines on account of the imposed, increasingly stringent, emission regulations. Introduction of cooled (exhaust) gas into the combustion chamber results in dilution of the air-charge by replacing O_2 with the non-reacting CO_2 and H_2O. Consequently, the in-cylinder gas mixture and the gas temperatures of the cycle are reduced. As a result, NO_x emissions are reduced too, aided by the lower oxygen availability since EGR in a diesel engine replaces oxygen, and so promotes a slight enrichment of the mixture. However, the usual ECU strategy during transients aims at shutting down the EGR valve in order to help build-up the air–fuel ratio and boost pressure, and limit intolerable

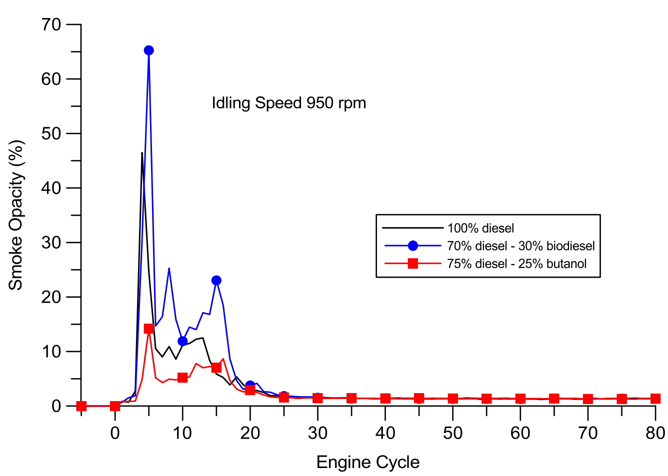


Fig. 6. Development of smoke opacity during hot starting of a medium-duty turbocharged diesel engine for neat diesel, Bu25 and B30 fuel blends [57].

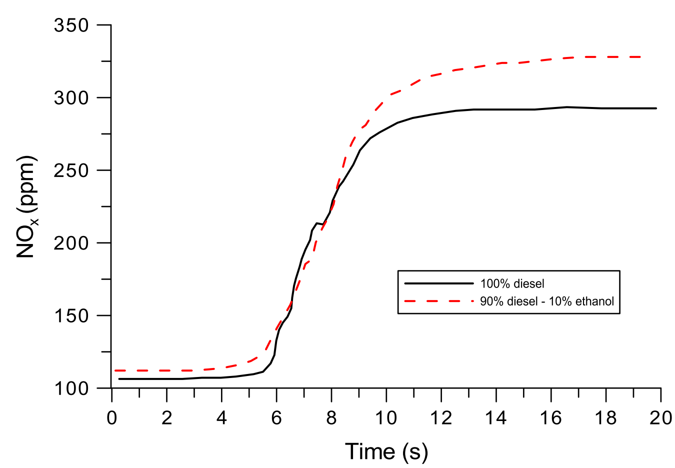


Fig. 8. Smoke opacity and NO_x development during a 26–90 Nm load increase transient event at 1661 rpm for neat diesel and E10 blend (experimental results adapted from Armas et al. [49]).

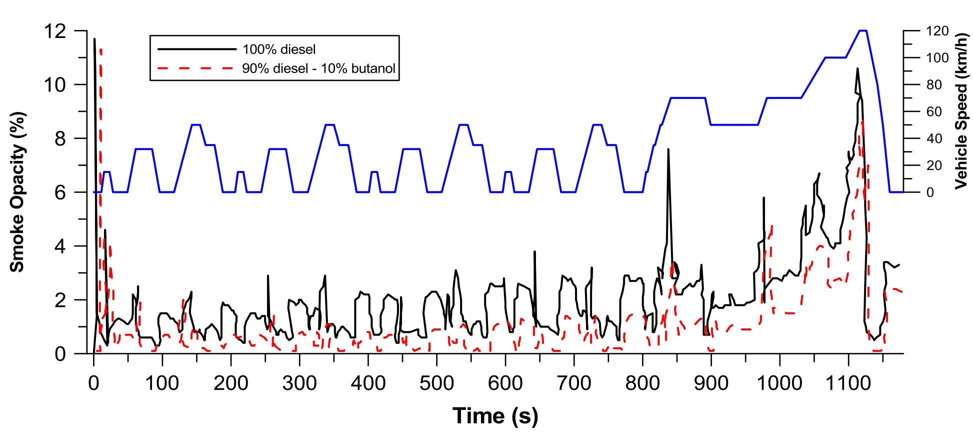


Fig. 7. Development of smoke opacity during the NEDC for neat diesel and a Bu10 blend of a passenger car diesel engine (experimental results adapted from Kozak [59]).

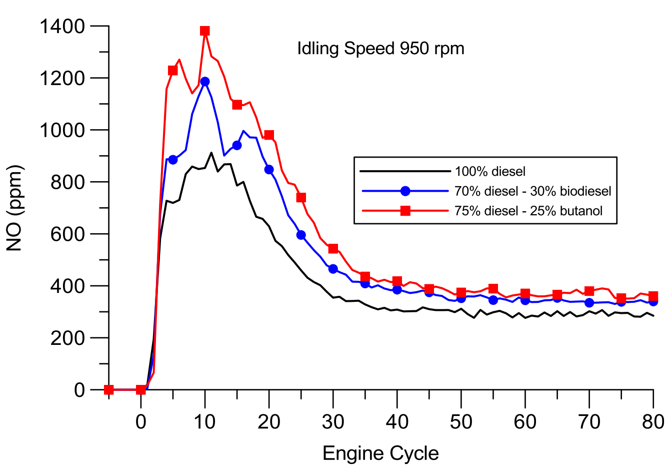


Fig. 9. Development of NO response during hot starting of a medium-duty turbocharged diesel engine for neat diesel, Bu25 and B30 fuel blends [57].

smoke emissions [11]. It is not surprising then that during this phase, which is experienced continuously during daily driving, an overshoot of nitrogen oxides is generally noticed. On the other hand when decelerating, very little amount of fuel is injected, resulting in a sharp decrease of NO_x emissions. During cruising, the EGR valve is open until its set point value and consequently NO_x emissions are successfully controlled [11].

Fig. 8 illustrates instantaneous NO_x concentration during the same load increase of Fig. 3 of a passenger car engine. However, a different trend is now established, with higher nitrogen oxides emitted throughout the whole transient event from the ethanol blend. Similar results have been reported by Rakopoulos et al. [55] for *n*-butanol/diesel blends during various medium-duty diesel engine accelerations (see also the collective results in Table 3). Likewise, Rakopoulos et al. [57] found that a Bu25 blend emitted higher NO (in ppm) during hot starting compared with the neat diesel operation, with representative results reproduced in Fig. 9. A further finding from the latter study concerned the development of combustion itself. It was revealed that the *n*-butanol blend behaved equally stable as the neat diesel fuel operation despite its lower cetane number, while, oddly enough, a higher degree of combustion instability was experienced by the biodiesel blend. On the other hand, Fanick [47] and Löfvenberg (downstream the DPF) [54] measured lower cumulative NO_x emissions during transient cycles when ethanol was added in the fuel blend, while Kozak [59] concluded that his Bu10 blend produced similar NO_x with the reference diesel operation during the NEDC.

There are several factors that contribute towards a reduced NO_x emission profile and various others that act towards an increased one, when either alcohol is added in the fuel blend, weighing more or less on the one or the other side, depending on the type of blends and the specific engine calibration and transient testing.

In particular,

- the alcohols' higher heat of vaporization (particularly ethanol's) with respect to diesel fuel, which means that a smaller amount of heat is available for the increase of the gas temperature since a larger amount of heat has been already consumed for the evaporation of the liquid blend,
- the lower C:H atom ratio of alcohols, which is expected to lower the adiabatic flame temperature [70],
- the fact that fuel injectors operate on a volumetric rather than gravimetric basis, which means that if a diesel fuel-tuned engine runs on alcohol/diesel fuel blends, a smaller mass of fuel will be injected, which is less likely to promote NO_x emissions as it is expected to lower the fuel–air equivalence ratio Φ and decrease the local gas temperatures, and
- the increased fuel leakage losses in the (mechanical) fuel pump owing to the lower kinematic viscosity of alcohols compared with the neat diesel fuel, which lead to lower injection pressures and, hence, mass of injected fuel,

all of those act in favor of reduced combustion temperatures – directly or indirectly through the lower local value of fuel–air equivalence ratio – hence lower NO_x emissions.

In contrast, there are several other factors that act towards higher NO_x liability relative to the conventional diesel fuel operation, namely

- the lower alcohol cetane number, which increases accordingly the ignition delay, hence the pressures and temperatures induced,
- the significantly higher oxygen availability, which is particularly influential during the early turbocharger lag cycles where the engine is starved from the required air-supply, means that local conditions are nearer to stoichiometric compared to the neat diesel fuel operation. This fact may not be of that dramatic importance during steady-state operation, but can prove quite influential during transients, particularly during the crucial turbocharger lag cycles when the fuel–air equivalence ratio is expected to be higher than unity. The underlying mechanism here is the promoted increase in the adiabatic flame temperature, which is well known to peak around stoichiometric conditions [70]. In other words, for the duration of the turbocharger lag, whereas during diesel combustion Φ might be well above unity, for alcohol/diesel combustion the excess oxygen inherent in the blend may lead to lower Φ values that are now closer to stoichiometry, and hence promote higher gas temperatures.
- the ECU calibration may dictate a different (advanced) injection strategy (longer injection pulse-width) based on the lower heating value of alcohols, if an engine that is tuned for neat diesel fuel operation is required to run on ethanol or normal butanol blends. By so doing, an increase in the premixed phase is observed (as is also the case with the lower CN), which increases accordingly the total residence time in the cylinder, and more importantly the pressures and temperatures during diffusion combustion. The reason for the increase in the premixed-portion of combustion lies in the fact that when the fuel in injected earlier in the cylinder, the surrounding conditions are less favorable for mixture preparation, particularly so for alcohol blends that are inherently characterized by lower ignitability,
- Lastly, an essential (actually, often prevailing) factor for the NO_x emissions behavior in modern engines is the exhaust gas recirculation (EGR) system. Owing to the lower energy density of oxygenated fuels, when an engine that has been calibrated for neat diesel fuel operation runs on alcohols (or biodiesel), higher fueling is required to achieve the demanded torque/vehicle speed (see, for example, the right-axis in Fig. 4). Since fueling is one of the inputs of the engine calibration maps, an increase in the air-mass flow set-point is experienced, hence a lower EGR rate is established that, in turn, escalates the in-cylinder temperatures and NO_x emissions [60,71].

It is the synergistic effect of all the above factors that produces the negative trends depicted in Figs. 8 and 9 for the discrete transient schedules examined, or the positive values reported by other researchers (summarized in Tables 2 and 3 by research group and transient schedule examined). In any case, it seems that the NO_x emission trend with alcohol/diesel fuel blends is not fully clear (similar conflicting results have been reached during steady-state experimentation), and probably not fully understood. More extensive testing is required in this field in order to

identify the influential factors, e.g., engine technology (fuel injection system) or transient schedule that prevail. As regards to the latter one, Armas et al. [49], reviewing various (steady-state) results, concluded that at light loads the use of ethanol/diesel blends has, in general, been found to produce benefits as regards NO_x with respect to diesel fuel, whereas at higher loading (as is the case with Figs. 8 and 9) the emission pattern seems to reverse. In support to these comments, Miers et al. [52] investigating the performance of a passenger car during two different driving cycles (UDDS and HWFET) found that during the urban (hence low-load and low-speed) UDDS, an increasing *n*-butanol blend ratio slightly decreased NO_x emissions (in g/km). On the other hand, during the highway (hence high-load and high-speed) HWFET cycle, a completely different trend was noticed, with noteworthy NO_x emission increases of the order of 25% for a Bu40 blend relative to the neat diesel fuel operation. In order to substantiate this finding, which is in agreement with similar observations from biodiesel blends [71], the fundamental causes for NO_x emission production need to be considered.

The reasons for the apparent *n*-butanol (and alcohol in general) higher NO_x liability with increasing cycle power lies in the primary NO_x production mechanism. For a diesel engine, increasing power means higher amount of injected fuel, which in turn raises the fuel–air equivalence ratio to a higher level, subsequently increasing (peak) flame temperatures (as long as Φ is maintained lower than unity, which is not always the case during abrupt transients). Likewise, a more aggressive cycle is characterized by more frequent and abrupt accelerations or load increases. The latter, as was illustrated in Fig. 1, pave the way for higher NO_x too, owing to the harsher (or more frequent) turbocharger lag phases and the lower EGR rates they induce [11].

The previously mentioned arguments, particularly those regarding the effects of EGR, underline the need for a revised engine calibration when a different (biofuel) blend is applied. For example, Magand et al. [60] found that when the ECU is appropriately re-adjusted to cater for the different physical and chemical properties of their E20 blend (most notably the lower LHV), the initially high NO_x penalty of the order of 60% relative to the reference diesel fuel was totally reversed into an impressive benefit of almost 22%, without sacrifice in the PM reduction.

4.1.3. Carbon monoxide and hydrocarbons

With the exception of the post-DOC measurements reported by Frank et al. [46], Löfvenberg [54] and Armas et al. [64] (the former two during transient cycles, the latter during a cold starting event), CO emissions seem to follow in general the trend of their PM/smoke counterparts (see the results in Tables 2 and 3). This fact can be collectively attributed to the same physical and chemical mechanisms affecting almost in the same way, at least qualitatively, the net formation of these two pollutants. More precisely, it is the excess oxygen in the fuel blend that aids the in-cylinder oxidation of CO to CO_2 that is most probably responsible for this behavior. As regards the reverse post-DOC trend, it is speculated that the experience from similar biodiesel measurements can prove illuminating. Owing to the alcohols' oxygen content, hence lower energy content and higher heat of evaporation, when an engine that is tuned for diesel combustion operates with an alcohol/diesel blend, lower exhaust gas temperatures are experienced [7,52] owing to the overall leaner operation; the latter is expected to adversely affect the oxidation catalyst's efficiency (and also the operation of other engine subsystems, such as, for example, the variable geometry turbocharger or the regeneration rate of the diesel particulate filter), as has actually been the case for biodiesel blends [71–73]. It seems then that this must be the underlying mechanism behind the trend observed in the alcohol results reported in [46,54,64], although no solid proof exists (i.e., there is no measurement of the DOC's efficiency), and further experimentation is definitely required.

Despite the clear PM and pre-DOC CO emission benefit with ethanol blending (as regards fully warmed-up operation), hydrocarbon emissions during transients (as has also been the case during steady-state operation) present a dissimilar behavior, even though the absolute values of the emitted HC (and CO) from modern diesel engines are, in any case, small. This has been the almost unanimous finding from all transient experimentations so far, as these are demonstrated in Tables 2 and 3 for ethanol and *n*-butanol/diesel blends, respectively.

In general, the primary sources of HC production are located around the perimeter of the reaction zone, where the mixture is too lean to burn, in the fuel retained in the injection nozzle sac (fuel leaving the injector nozzle at low velocity, late in the combustion process), in the spray cores and tail. Hydrocarbon emissions are greatly influenced by load, ambient conditions, turbocharging and fueling system. Hence, the most probable causes for this compelling increasing HC trend with the addition of ethanol or *n*-butanol in the fuel blend can be attributed to [15,23]:

- the higher heat of vaporization of the alcohol blends causing slower evaporation hence slower and poorer fuel–air mixing,
- the increased spay penetration causing unwanted fuel impingement on the chamber walls (and so flame quenching) and cushioning in the ring land areas, and to the increase with alcohols of the so called 'lean outer flame zone' where flame is unable to exist,
- the non-homogeneity of the blend (particularly the ethanol/diesel one) causing increased leanness of the mixture in certain regions inside the cylinder, particularly during low-load operation when the mixture is already lean enough, or during cold starting [64],
- the late escape into the cylinder of the fuel left in the nozzle sac volume, because with the addition of alcohols this is easier evaporated (as heated) and 'slipped' into the cylinder (at low velocity, late in the expansion stroke).

Moreover, all the above discrepancies are expected to enhance during transients, particularly during the first turbocharger lag engine cycles, where the inconsistency between the increased fueling and the still deficient air-supply is prominent.

As a result of the speculated oxidation catalyst's lower effectiveness with biofuel blends, these HC increases are expected to become more pronounced during the cold-started transient schedules or the cold-started runs of the driving cycle. Indeed, Miers et al. [52] found that during the (hot) HWFET cycle, the emissions of both HC and CO did not show any particular deviation from the neat diesel oil case, whereas during the cold-started runs they proved way more polluting. Likewise, Kozak [59] measured higher HC and CO increases (both instantaneous and cumulative) with *n*-butanol relative to neat diesel oil during the cold-started urban part of the NEDC compared with the respective ones during the whole driving cycle.

Interestingly, Miers et al. [52] found that although the pre-DOC exhaust gas temperatures were lower when *n*-butanol was added into the fuel blend, their post-DOC counterparts were measured higher, probably owing to the greater amount of emitted HC and CO, which resulted in higher reactivity inside the oxidation catalyst. This fact is very promising for downstream catalytic converters in the form of DPF or NO_x adsorbers, which rely on high temperatures for their regeneration.

4.1.4. Non-regulated emissions

Non-regulated emissions from diesel engines correspond to organic and air–toxic pollutants such as:

- Carbonyl compounds, formed by aldehydes (formaldehyde, acetaldehyde, acrolein, propionaldehyde, etc) and ketones (e.g., acetone). Carbonyls account for most of the ozone-forming potential of organic gases
- benzene, which is a colorless, flammable, carcinogenic aromatic hydrocarbon of the type C_6H_6
- naphthalene, which is a volatile, crystalline, aromatic, white, solid hydrocarbon of the type $C_{10}H_8$, comprising of two benzene rings sharing a pair of carbon atoms
- alcohols, i.e., organic compounds with a hydroxyl group (–OH) bound to a carbon atom of an alkyl or substituted alkyl group, having the general type $C_nH_{2n+1}OH$
- polycyclic aromatic hydrocarbons, also known as PAHs; these are compounds similar to benzene but consisting of four, five or six rings joined together
- nitrated polycyclic aromatic hydrocarbons, also known as nPAHs, either directly emitted during combustion or formed from the parent PAHs by atmospheric OH or NO_3 radical initiated reactions

Non-regulated emissions are usually more difficult to measure, owing to their very small concentration (of the order of a few ppm), whereas their detailed mechanism of production is not absolutely clear.

All four studies focused on alcohol/diesel fuel blends impacts on unregulated emissions during transients [45,47,50,63] agree that the amount of emitted carbonyl compounds increases when ethanol or normal butanol is added into the fuel blend, thus confirming the few available results during steady-state operation e.g., [48,74]. A comparative study by Ballesteros et al. [63] revealed that it is the ethanol/diesel fuel blends that are responsible for the highest increases, with their *n*-butanol counterparts contributing to a smaller extent. Moreover, Tang et al. [50] found that BTEX (benzene, toluene, ethylbenzene, xylene, and 1,3 butadiene), PAHs and nPAHs all behaved similarly during the FTP when the engine was running on an ethanol/diesel fuel blend, i.e., an increasing trend compared with the reference diesel fuel was measured. PAH and nPAHs increases were, in general, noticed by Fanick too [47], when ethanol was added in the fuel blend. In the latter study, it was also reported, and this is actually a very promising fact, that no additional compounds were present in the alcohol-blend exhaust when the emissions were compared with the exhaust from the baseline fuel. All these measurements correspond to engine-out emissions, whereas the effect of

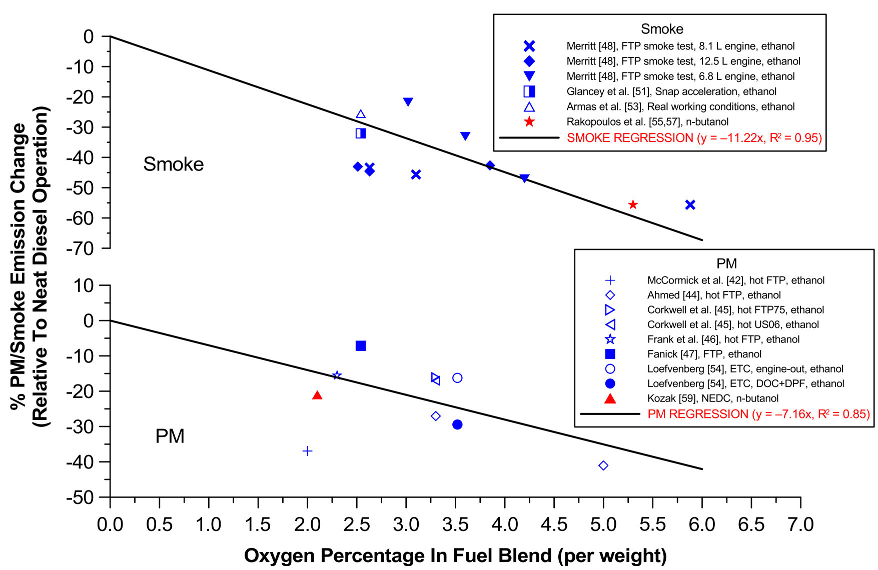


Fig. 10. Collective PM (lower sub-diagram) and smoke (upper sub-diagram) emission benefits from ethanol and *n*-butanol/diesel fuel blends combustion during transient schedules (for those studies where no relevant information was available, it was assumed that the oxygen content of the reference diesel fuel was zero; for Merritt et al. [48], average values are taken from the three components of the FTP smoke test; for Rakopoulos et al. [55,57], average-cumulative values are taken from three accelerations and one hot starting).

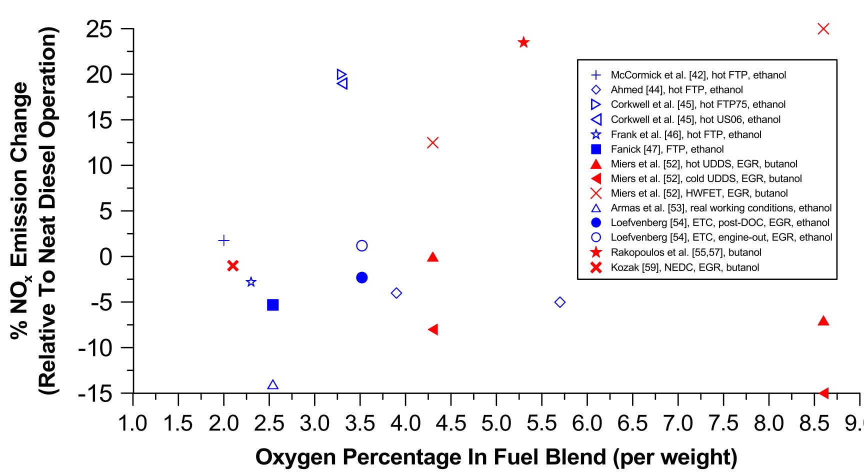


Fig. 11. Collective NO_x emissions change from ethanol and *n*-butanol/diesel fuel blends combustion during transient schedules (for those studies where no relevant information was available, it was assumed that the oxygen content of the reference diesel fuel was zero; for Rakopoulos et al. [55,57], average-cumulative NO (and not NO_x) values are taken from three accelerations and one hot starting).

either DOC or DPF was found to vary depending on each fuel blend tested [50,63]. In any case, non-regulated exhaust findings require further testing in order to provide a possibly unambiguous trend. Furthermore, the use of ethanol or *n*-butanol in fuel blends results also in their release into the atmosphere, where the alcohols will undergo a photochemical oxidation initiated by the OH radical. Therefore, an assessment of their atmospheric chemistry and environmental impact is necessary [63,75].

4.1.5. Overall results

From Tables 2 and 3, a clear decreasing PM/smoke trend is established when ethanol or *n*-butanol is added in the fuel blend relative to the neat diesel fuel operation. For the rest of the regulated pollutants, however, no such unique trend can be identified, except for the consistent, and usually significant, increase of HC. Contradicting results hold for CO_2; the few studies that measured carbon dioxide emissions concluded that these may increase or decrease, usually by a small percentage, relative to the reference operation.

Further, Figs. 10 and 11 illustrate graphically the results from Tables 2 and 3 concerning PM/smoke (Fig. 10) and NO_x (Fig. 11) emission changes with alcohol/diesel blends during transient cycles or real working conditions. From Tables 2 and 3 only those results where the oxygen content of the fuel blend originated exclusively from the alcohols are taken into account, i.e., when biodiesel was also added in the fuel blend the relevant data were not included in Figs. 10 and 11. The same holds true for the cases where the reference fuel was biodiesel-blended; these results were not included as they obviously mask the effect of the alcohol addition. In order to demonstrate in the same figure the effects from both alcohols studied, the oxygen content (per weight, w/w) of the fuel blend was chosen as the independent variable.

A very intriguing fact is revealed in the linear best-fit regression curves in Fig. 10, i.e., a rather high degree of statistical significance of the PM data with the fuel-bound oxygen is evident, implying that from the arguments raised in Section 4.1.1.3 this is indeed the decisive factor, as has also been argued in [76,77] during steady-state operation. It is noted that although the diesel oxidation catalyst has a positive, but rather moderate, effect on PM, both engine-out and post-DOC measurement values are included in Fig. 10. On the whole, the linear best fit PM curve for the alcohol/diesel fuel blends is $y=-7.16x$, with x being the per weight (w/w) oxygen content in the fuel blend and y the PM percentage benefit relative to the reference diesel operation; the data-set includes 10 measurements from 7 different studies/engines. If only the heavy-duty engines are taken under consideration, the data significance remains the same, but the PM benefit is now somewhat greater ($y=-7.61x$) as is also summarized in Table 4. If the studies that focused on the non-legislated smoke are taken into account (upper sub-diagram of Fig. 10), both the statistical significance ($R^2=0.95$) and the benefit over the reference operation are higher. For the latter case, there are 12 available measurements, however from only four studies.

From these arguments then, it can be concluded that an alcohol/diesel fuel blend with 3.3% w/w oxygen content (roughly 10% ethanol or 16% *n*-butanol *v*/*v* in the final blend, assuming zero oxygen for the neat diesel fuel) is expected to decrease PM by 24%, while a 5% w/w oxygen content (approximately 15% ethanol or 24%

Table 4
Summarization of best-fit linear curve coefficients *A*, coefficients of determination R^2 and standard errors for PM, smoke and pre-DOC CO benefits during transient/driving cycles with ethanol or *n*-butanol added in the fuel blend (best-fit curve: $y=Ax$; x is the per weight oxygen content, assuming zero oxygen for the neat diesel, and y the percentage emission benefit relative to neat diesel operation).

	PM	Smoke	CO
All data	$A=-7.16$ $R^2=0.85$ Std. error=0.99 Count=10 (7 studies/7 engines)	$A=-11.22$ $R^2=0.95$ Std. error=0.79 Count=12 (4 studies/6 engines)	–
All ethanol data	$A=-7.03$ $R^2=0.85$ Std. error=1.05 Count=9 (6 studies/6 engines)	$A=-11.38$ $R^2=0.94$ Std. error=0.91 Count=11 (3 studies/5 engines)	–
All heavy-duty engines	$A=-7.61$ $R^2=0.85$ Std. error=1.28 Count=7 (5 studies/5 engines)	$A=-11.22$ $R^2=0.95$ Std. error=0.79 Count=12 (4 studies/6 engines)	$A=-3.74$ $R^2=0.76$ Std. error=0.94 Count=6 (5 studies/5 engines)

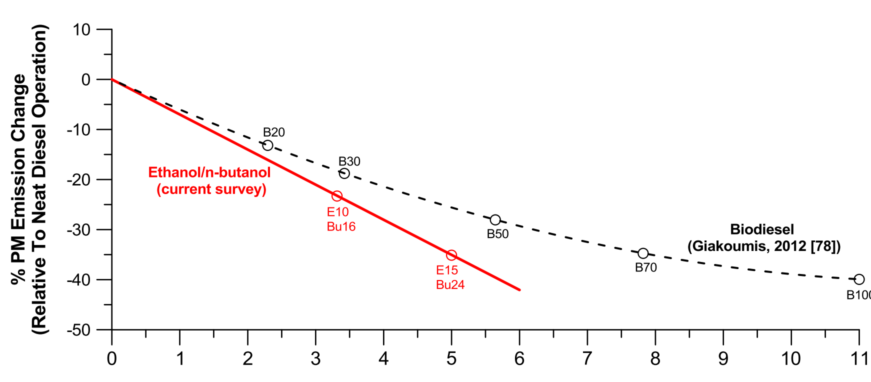


Fig. 12. Statistical results of ethanol or *n*-butanol/diesel blends PM emission benefit over neat diesel operation (solid red line) in comparison with biodiesel blends (discontinuous black line) during transient cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

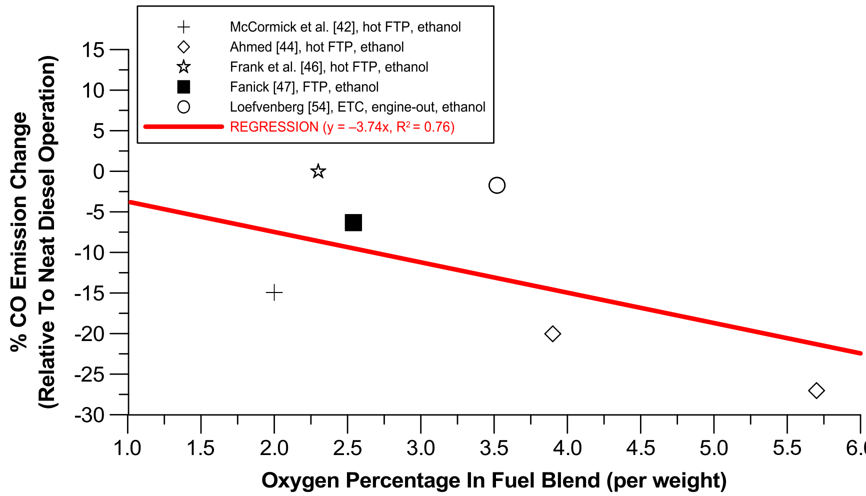


Fig. 13. Collective engine-out CO emissions change from ethanol/diesel fuel blends combustion during heavy-duty, engine-dynamometer cycles (for those studies where no relevant information was available, it was assumed that the oxygen content of the reference diesel fuel was zero).

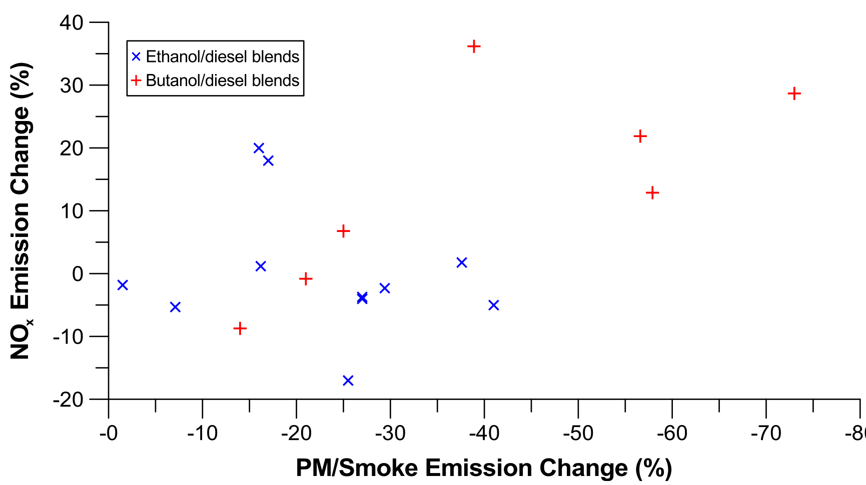


Fig. 14. PM/NO_x trade-off from ethanol and *n*-butanol/diesel fuel blends combustion during transient schedules (smoke values instead of PM are used for those studies that did not measure PM).

n-butanol *v*/*v*) reduces the amount of emitted PM relative to the neat diesel fuel operation by 36%. In contrast, the respective benefit from biodiesel combustion assumes a comparable value of 36% when a B70 blend (i.e., 7.8% w/w oxygen content) is applied [78]. Some other representative, comparative values are provided in Fig. 12. These very interesting data prove that when comparing different biofuels, it is not the amount of oxygen alone that is responsible for higher or more efficient in-cylinder soot oxidation rate. There are other, inherent in the molecule of each fuel, contributing parameters (e.g., flame structure and velocity, the balance between premixed and diffusion combustion as was also pinpointed in Section 4.1.1 etc) that ultimately differentiate one biofuel from the other and produce the final benefit over the reference diesel fuel operation. Hence, it is the attributes inherent in the combustion of alcohols, most notably their propensity towards premixed-flame combustion combined with the hydroxyl group (–OH), that differentiate substantially the PM emission benefit over biodiesel combustion, increasing the capacity for reduced exhaust gas smokiness over the reference diesel fuel operation. On the other hand, it has been shown [79] that the methyl esters during biodiesel blends combustion undergo decarboxylation, which yields a CO_2 molecule directly from the ester. This results in the oxygen in the fuel being used less effectively to remove carbon from the pool of soot precursors.

For NO_x on the other hand (Fig. 11), as has also been the case with biodiesel blends [71,78,80], the alcohol/diesel blend data are scattered and controversial, indicating that there are many other critical parameters apart from the oxygen content that are responsible for the overall emission behavior; hence no statistically significant correlation can be established (R^2=0.02). The same holds true, in general, for CO and HC. However, there seems to be a notable exception as regards the engine-out, heavy-duty, engine-dynamometer measurements of CO, which present a promising value of R^2=0.76 or even 0.87 if only the FTP (hot-started runs) are taken into account, although the dataset is very small to suggest an unequivocal trend. These are documented in Fig. 13 and Table 4.

Lastly, Fig. 14 demonstrates the, well established during neat diesel fuel steady-state operation, contradicting behavior (trade-off) between PM and NO_x. Actually, this is one of the main benefits when employing biofuels and particularly alcohols. The significant potential for PM reduction offers greater flexibility in controlling NO_x by applying other measures, such as elevated EGR [81].

4.2. Combustion noise

From an acoustic point of view, the diesel engine, being a very complex system comprising various dynamic forces acting on a

structure of varying stiffness, damping and response characteristics, remains by far inferior to its gasoline counterpart. Particularly for diesel-engined vehicles, the unpleasant combustion 'knock' is also a matter of discomfort for passengers and pedestrians. The three primary sources of noise generation in a diesel engine are: gas-flow, mechanical processes, and combustion [82,83]. Gas-flow noise, which is usually low frequency controlled, is associated with the intake and exhaust processes, including turbocharging. Mechanical noise comprises both rotating and reciprocating engine components contribution, which originates from inertia forces causing piston slap, and from gears, tappets, valve trains, timing drives, fuel injection equipment and bearings. The mechanism behind the third source of noise, namely combustion noise, lies in the (high) rate of cylinder pressure rise, mainly after the ignition delay period, which causes discontinuity in the cylinder pressure frequency spectrum and increase in the level of the high-frequency region, thus resulting in vibration of the engine block and, ultimately, in combustion noise radiation (the characteristic diesel combustion 'knock'). This combustion noise radiation manifests itself in the frequency domain from a few hundred up to a few thousand Hz.

There is only a handful of works available regarding alcohol effects on combustion noise radiation during steady-state diesel engine operation (directly, or indirectly through the more easily computed 'surrogate' property of cylinder pressure rise rate $dp/d\varphi$); they are all limited to ethanol [60,84,85], with no available results for *n*-butanol blends. They report increases in the emitted combustion noise when ethanol was added into the fuel blend, owing to the lower ethanol cetane number that increased accordingly the ignition delay period, hence the premixed combustion phase.

On the other hand as regards transients, the only available direct result regarding alcohol impacts on combustion noise development has been reported by Giakoumis et al. [62]. This is depicted in Fig. 15 that illustrates noise development during a medium-to-high speed, low-load acceleration of a medium-duty engine running on *n*-butanol/diesel fuel blends. The evolution of peak cylinder pressure is provided in the left sub-diagram, which reveals that the diesel/*n*-butanol blend exhibited higher peak cylinder pressures compared to the neat diesel fuel operation. The radiation of combustion noise was also higher for the diesel/*n*-butanol blend (right sub-diagram of Fig. 15), confirming the steady-state ethanol results. The apparent reason for this

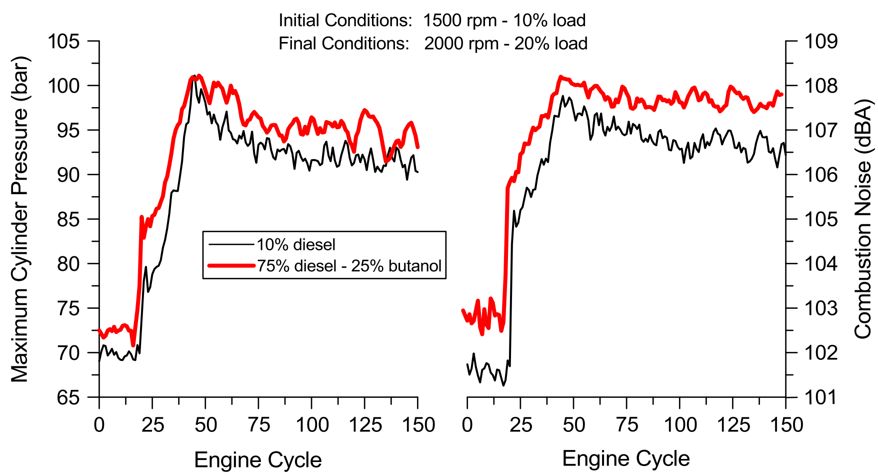


Fig. 15. Development of maximum cylinder pressure (left) and combustion noise radiation (right) during a low-load acceleration of a medium-duty, turbocharged diesel engine for neat diesel and Bu25 fuel blends [62].

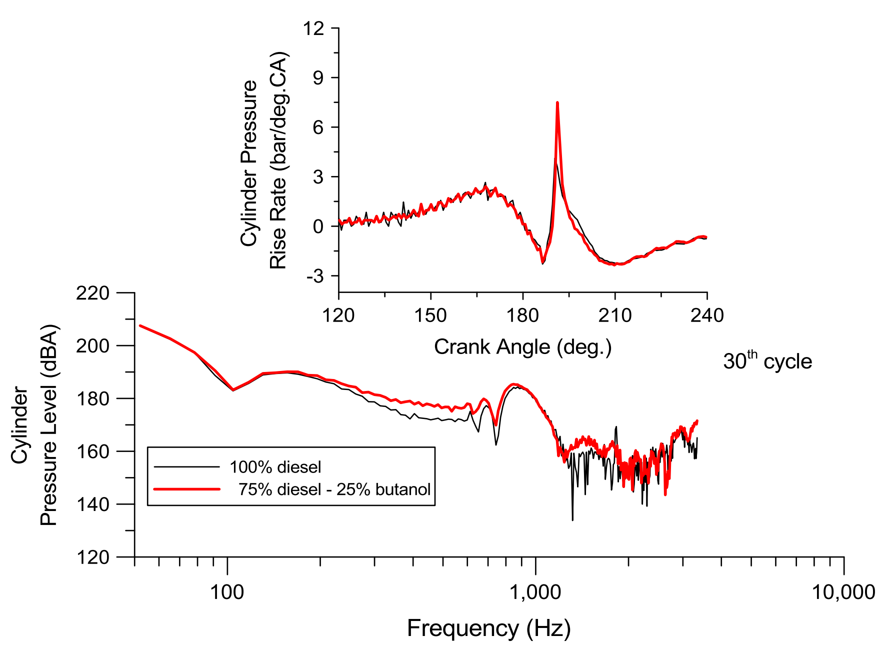


Fig. 16. Cylinder pressure rise rate and sound level during the 30th cycle of the acceleration test of Fig. 15 [62].

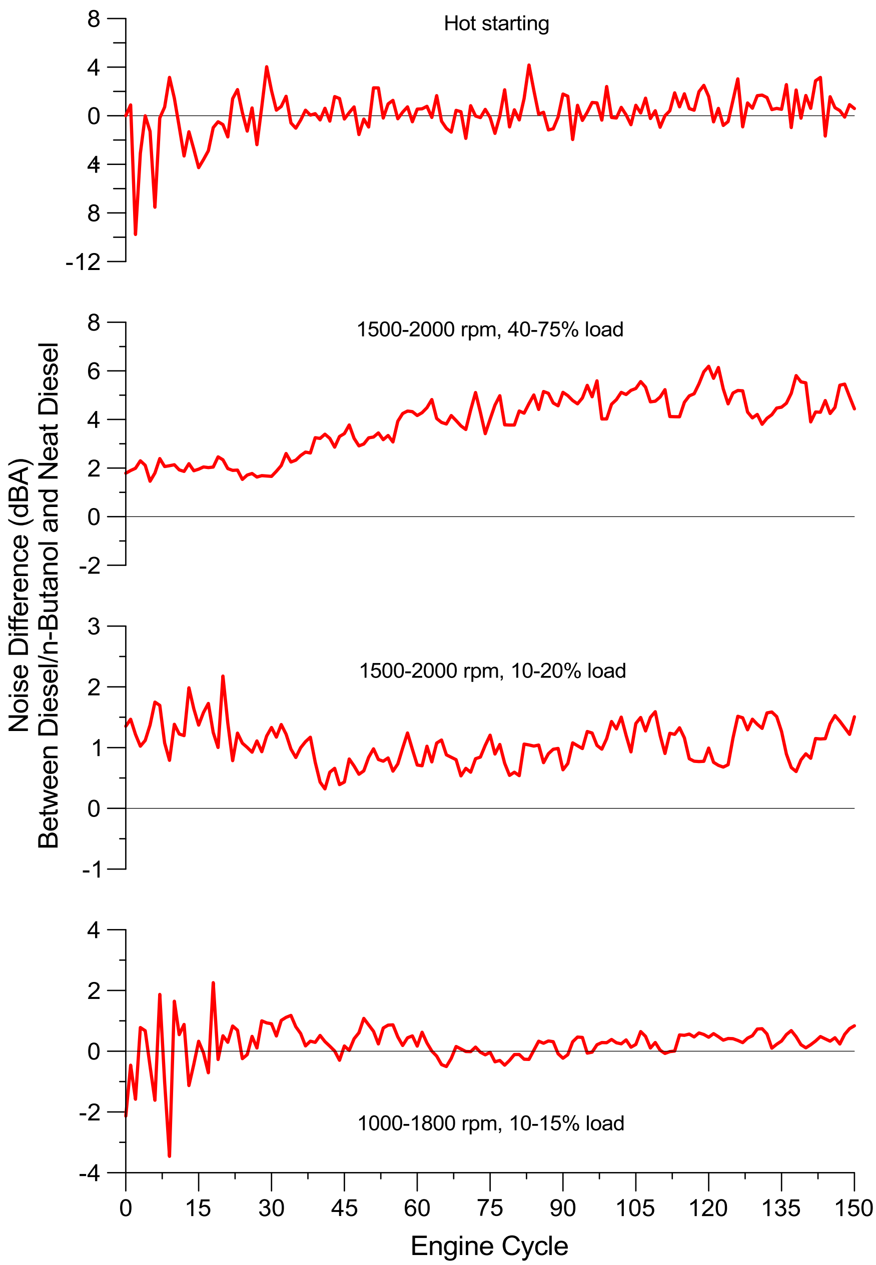


Fig. 17. Development of combustion noise difference between diesel fuel and a Bu25 blend throughout three acceleration tests and one starting event [57,62] (positive noise difference values indicate noisier operation of the Bu25 blend).

behavior lies in the normal butanol lower cetane number, which lengthened the ignition delay and increased accordingly the cylinder pressure rise rate (upper sub-diagram of Fig. 16).

The higher noise emission for the *n*-butanol/diesel fuel blend was measured up to 2.2 dBA during the transient event of Fig. 15 compared with the neat diesel fuel operation, and was experienced during the whole acceleration event. This can be further established in the lower sub-diagram of Fig. 16 that illustrates the respective cylinder pressure spectra for a representative engine cycle during the acceleration. The higher amount of emitted noise for the diesel/ *n*-butanol blend is apparent in Fig. 16 during the critical, for the combustion excitation forces, region between 500 Hz and a few kHz.

Further collective combustion noise results from this transient (acceleration) research [62] are reproduced in Fig. 17, substantiating the previous arguments. In contrast, during starting the *n*-butanol blend showed no clear acoustic trend over the reference diesel operation [57]. Judging from these *n*-butanol transient results and the few steady-state ethanol findings, it is postulated that the (lower-cetane-number) ethanol/diesel fuel blends will behave even noisier during transients. In a recent research by Armas et al. [64] on engine starting with both ethanol and *n*-butanol blends, although there was no direct measurement/estimation of combustion noise, the ‘surrogate’ values of $dp/d\varphi$ corroborate this speculated ‘noisier’ ethanol–diesel fuel operation.

Although combustion noise is not among the regulated emissions, the emergence of new promising diesel combustion technologies, such as low temperature combustion and PCCI that are based on lower cycle temperatures for simultaneously limiting soot and NO_x emissions, is expected to pose a detrimental effect on combustion noise, owing to the higher portion of premixed combustion that these lower cycle temperatures induce [86]. Hence, it is anticipated that the simultaneous use of alcohol/diesel fuel blends and low-temperature combustion diesel technology will further deteriorate the radiated combustion noise [87,88].

5. Conclusions

A review was conducted of the literature concerning emissions of diesel engines when running on ethanol or *n*-butanol/diesel fuel blends during transient conditions. The main mechanisms of transient emissions were identified and discussed for all exhaust pollutants, with many of those mechanisms being interrelated with the inherent discrepancies observed during transients, most notably turbocharger lag. The most important conclusions derived are summarized as follows:

1) With only few exceptions, the surveyed transient studies (either those that focused on discrete transient events or those that investigated transient/driving cycles), reported a decreasing trend in PM and engine-out CO, and an increasing trend in unburned HC emissions when ethanol or *n*-butanol is added in the fuel blend. Hence, the results reached during steady-state conditions are confirmed.
2) For PM emissions, the high oxygen concentration in the alcohol-blend, which aids the soot oxidation process (most importantly during the critical turbocharger lag cycles), has been identified as the key contributor for the benefits relative to neat diesel fuel operation, at least as regards (fully) warmed-up engine conditions. Other notable causes are the lower stoichiometric air–fuel ratio of alcohol–diesel blends, the absence of aromatic and sulfur compounds, and the lower induced EGR ratio resulting from the alcohols' smaller value of LHV. During cold starting on the other hand, the results from the two available studies report both considerable increases and decreases in the smoke opacity when ethanol was added in the fuel blend.
3) The analysis of the available transient PM/smoke results revealed that there is a statistical significance ($R^2=0.85$) between PM reduction capability and oxygen content (compared with the neat diesel fuel operation), although the available data-set is not adequately large. Even higher degree of significance ($R^2=0.95$) was established between smoke reduction capability and alcohol-diesel blend oxygen content.
4) An interesting statistical comparison between alcohols and biodiesel revealed that alcohol–diesel blends behave more efficiently in reducing the exhaust smokiness than biodiesel ones, even when the oxygen content in the fuel blend is the same.
5) On the other hand for NO_x emissions, the trend is not clear, with both increases and decreases being reported depending on the specific alcohol percentage, the engine calibration, and the transient schedule's characteristics. Specifically, the exact amount of the emitted NO_x emerges as the competitive result between various factors, which act in favor of higher local gas temperatures (e.g., lower alcohol cetane number, lower EGR ratio (see point 8 below)) and various others that act in contradiction (e.g., higher alcohol heat of evaporation and lower C:H atom ratio), with the higher amount of available oxygen playing also a vital role.
6) Although the use of ethanol or *n*-butanol/diesel fuel blends alone might not prove sufficient to achieve current or future PM emission levels (that is without the need for exhaust gas after-treatment devices), the inherent capability of alcohols to decrease PM by a large percentage provides higher flexibility in controlling NO_x emissions by using a variety of other (internal) measures, such as elevated EGR rates.
7) The (speculated) oxidation catalyst's decreased overall efficiency owing to the lower exhaust gas temperatures of alcohol-blends seems to be responsible for even higher vehicle-out unburned HC emissions. Concerning CO, the positive (i.e., lower) pre-DOC results may be totally reversed when post-DOC measurements are studied. The engine-out CO emission reductions from alcohol/diesel blends over neat diesel fuel operation have been found to correlate fairly well ($R^2=0.76$) with the oxygen content for the few heavy-duty, engine-dynamometer measurements available, particularly those that correspond to FTP hot runs.
8) Owing to the smaller calorific value of alcohols, when an engine being calibrated for neat diesel fuel operation runs on ethanol or normal butanol/diesel blends (as was actually the case in all the surveyed studies), a lower EGR rate is achieved, contributing towards an increase in NO_x emissions and decrease in PM with respect to the petroleum diesel fuel operation. Moreover, other engine subsystems such as the injection system, the variable geometry turbocharger, and the diesel particulate filter might be influenced. This crucial remark highlights the need for a revised calibration strategy when a diesel-tuned engine is required to run on ethanol, *n*-butanol or any other biofuel/diesel fuel blend.
9) The few studies that measured carbon dioxide emissions, concluded that these may increase or decrease with the addition of alcohols, usually by a small percentage, relative to the reference operation but without evident clear trend.
10) Carbonyl compounds show an increasing trend when ethanol is added in the fuel blend, and it seems that, at least, some of the other unregulated emissions (BTEX, PAHs, nPAHs) follow a similar trend. However, the experimental data-set for the unregulated pollutants is still narrow to identify possibly unequivocal trends.
11) There is only one reference as to the effect of alcohol/diesel blends on particle number and size distribution during transients (starting in particular). Hence, this subject matter constitutes an intriguing field for future research, bearing in mind that PM-reducing techniques (e.g., DPF or the use of biodiesel) have been found by many researchers to increase the number of the emitted (more toxic) nano-particles.
12) Combustion noise radiation during an acceleration transient event, such as those experienced continuously during daily driving, has been found to increase when *n*-butanol blend is applied. Although there are no results available for ethanol, it is strongly suspected that the trend is even more prominent. It appears that the alcohols' lower cetane number is responsible for this behavior, as it increases the ignition delay period and thus, the amount of fuel burned during the premixed phase. In any case, these transient results need further testing for confirmation as the available results are very limited.

The performance of the engine during fully-warmed up transients when ethanol or *n*-butanol are added in the fuel blend has been reported as normal. This is not the case, however, during cold starting where increased cranking period and rough engine operation has been experienced by all researchers. The lower cetane number of alcohols is responsible for this behavior, requiring additives or different (e.g., split or recalibrated) injection strategies for compensation.

Although biodiesel is nowadays considered the primary alternative fuel for diesel engines, ethanol, and normal butanol show promising emission results during real driving conditions, particularly with respect to PM reduction and hence the flexibility in controlling the PM/NO_x trade-off. Therefore, it is believed that they can be considered as further alternative options for compression ignition engines in the near future, at least for small (up to 20%) percentages in the fuel blend. However, issues related to the storage and stability for ethanol, and production rate/cost for *n*-butanol need first to be solved, with extensive durability and wear tests on various types of engines and injection systems being called for.

Appendix

Details of the papers/reports dealing with transient exhaust emissions with ethanol and *n*-butanol/diesel blends.

Table A
Details of the studies dealing with transient exhaust emissions with alcohol/diesel blends.

	Research group	Reference.	Year	Publication	Engine application	Engine MY or emission level	Alcohol (percentage)	Stability additive	Transient schedule	Reference fuel	Transient emissions	Instantaneous measu-rements	Notes/other fuels tested
1	Peterson and Reece	[41]	1994	ASAE	Heavy-duty	1994	Ethanol (10%)	No	Transient cycle (arterial)	Diesel/ REE10	PM, NO_x, CO, CO_2, HC	No	RME/REE
2	McCormick et al.	[42]	1997	Environmental Science and Technology	Heavy-duty	1989	Ethanol (6.5%)	n/a	Transient cycle (hot FTP)	Diesel No. 2	PM, NO_x, CO, HC	No	SME, octanol
3	Spreen	[43]	1999	Report	Heavy-duty	1991	Ethanol (10%, 15%)	Yes	Transient cycle (hot FTP)	Diesel No. 2	PM, NO_x, CO, HC	No	–
4	Ahmed	[44]	2001	SAE	Heavy-duty	1991	Ethanol (10%, 15%)	Yes (1–2%)	Transient cycle (hot FTP)	Diesel No. 2	PM, NO_x, CO, HC	No	–
5	Corkwell et al.	[45]	2003	SAE	Passenger car	2001	Ethanol (10%)	Yes	Transient cycles (hot FTP75, hot US06)	ULSD	PM, NO_x, CO, HC, carbonyls	No	–
6	Frank et al.	[46]	2004	SAE	Heavy-duty	2001	Ethanol (7%)	Yes	Transient cycle (hot FTP)	Diesel No. 1, No. 2	PM, NO_x, CO, CO_2, HC	No	F-T, SME/ DOC, DPF effects
7	Fanick	[47]	2004	Report	Heavy-duty	2002	Ethanol (7.7%)	Yes (0.6–1%)	Transient cycle (FTP)	Diesel	PM, NO_x, CO, HC, non-regulated	No	–
8	Merritt et al.	[48]	2005	SAE	Non-road	Tier II	Ethanol (7.7%, 10%, 15%)	Yes (1–2.6%)	FTP smoke test	Diesel No. 2	Smoke opacity	No	3 engines/ steady-state tests
9	Armas et al.	[49]	2007	SAE	Passenger car	≥ Euro 3	Ethanol (10%)	No	Engine load increase and cold starting	LSD	Smoke opacity, NO_x	Yes	–
10	Tang et al.	[50]	2007	Environmental Science and Technology	Heavy-duty	2001	Ethanol (7%)	Yes	Transient cycle (FTP)	Diesel No. 1, No. 2	Non-regulated	No	F-T, SME/ DOC, DPF effects
11	Miers et al.	[52]	2008	SAE	Passenger car	1999	*n*-Butanol (20%, 40%)	–	Transient cycles (UDDS,HWFET)	ULSD	NO_x, CO, CO_2, HC	No	–
12	Armas et al.	[53]	2009	Energy and Fuels	Non-road	n/a	Ethanol (7.7%)	Yes (0.62%)	Real working conditions	LSD	Smoke opacity, NO_x	Yes	–
13	Löfvenberg	[54]	2009	Report	Heavy-duty	Euro III	Ethanol (10%)	n/a	Transient cycle (ETC)	Diesel MK1/ RME5	PM, NO_x, CO, CO_2, HC	No	DOC, DPF effects
14	Rakopoulos et al.	[55]	2010	Energy	Medium-duty	Euro II	*n*-Butanol (25%)	–	Engine acceleration	LSD	Smoke opacity, NO	Yes	Biodiesel
15	Cheenkachorn and Fungtamasan	[56]	2010	Energy Sources Pt. A	Light-duty	n/a	Ethanol (5%)	No	Transient cycle (Bangkok driving cycle)	Diesel/ PME11	PM, NO_x, CO, CO_2, HC	No	–
16	Rakopoulos et al.	[57]	2011	Applied Energy	Medium-duty	Euro II	*n*-Butanol (25%)	–	Hot starting	LSD	Smoke opacity, NO, combustion noise	Yes	Biodiesel
17	Randazzo and Sodre	[58]	2011	Fuel	Passenger car	Euro 4	Ethanol (2%, 5%)	No	Transient cycle (NEDC)	Diesel/ SME20	PM, NO_x, CO, CO_2, HC	No	–
18	Kozak	[59]	2011	SAE	Passenger car	Euro 4	*n*-Butanol (10%)	–	Transient cycle (NEDC)	ULSD	PM, NO_x, CO, CO_2, HC, smoke opacity	Yes	Cold/hot results comparison
19	Magand et al.	[60]	2011	Oil and Gas Science and Technology	Passenger car	Euro 4	Ethanol (20%)	No	Transient cycle (NEDC)	F-T/ RME/ hexane	PM, NO_x, CO, CO_2, HC	No	ECU optimi-zation/ steady-state tests
20	Hulwan and Joshi	[61]	2011	Applied Energy	Medium-duty	n/a	Ethanol (20%, 30%)	No	Free acceleration	Diesel/JME	Smoke opacity	No	–

21	Giakoumis et al.	[62]	2012	IMechE (Part D)	Medium-duty	Euro II	*n*-Butanol (25%)	–	Engine acceleration	LSD	Combustion noise	Yes	Biodiesel
22	Ballesteros et al.	[63]	2012	Fuel	Passenger car	Euro 5	Ethanol (10%), *n*-Butanol (16%)	n/a	Vehicle acceleration	Diesel	Carbonyls	No	–
23	Armas et al.	[64]	2012	Fuel Processing Technology	Passenger car	Euro 5	Ethanol (10%), *n*-Butanol (16%)	No	Starting	LSD	Smoke opacity, NO_x, HC, CO, particle size distribution	Yes	Cold/hot results comparison

– n/a: Not available; LSD: low-sulfur diesel; ULSD: ultra low-sulfur diesel; REE10: 10% (*v*/*v*) rapeseed ethyl ester; RME5: 5% (*v*/*v*) rapeseed methyl ester; PME11: 11% (*v*/*v*) palm methyl ester; SME20: 20% (*v*/*v*) soybean methyl ester; F-T: Fischer–Tropsch; JME: Jatropha methyl ester.
– in Refs. [41,54,56,58,60,61], the tested fuel blend contained also biodiesel.

References

[1] Hansen AC, Kyritsis DC, Lee CF. Characteristics of biofuels and renewable fuel standards. In: Vertes AA, Qureshi N, Blaschek HP, Yukawa H, editors. Biomass to biofuels—strategies for global industries. Oxford: Blackwell Publishing; 2009.
[2] Tverberg GE. Oil supply limits and the continuing financial crisis. Energy 2012;37:27–34.
[3] Inventory of US greenhouse gas emissions and sinks: 1990–2009 (April 2011), US EPA #430-R-11-005.
[4] Markevicius A, Katinas V, Perednis E, Tamasaukiene M. Trends and sustainability criteria of the production and use of liquid biofuels. Renewable and Sustainable Energy Reviews 2010;14:3226–31.
[5] Komninos NP, Rakopoulos CD. Modeling HCCI combustion of biofuels: a review. Renewable and Sustainable Energy Reviews 2012;16:1588–610.
[6] Hansen AC, Zhang Q, Lyne PWL. Ethanol/diesel fuel blends—a review. Bioresource Technology 2005;96:277–85.
[7] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels in internal combustion engines. Progress in Energy and Combustion Science 2007;32: 233–71.
[8] Jin C, Yao M, Liu H, Lee C-F, Ji J. Progress in the production and application of *n*-butanol as a biofuel. Renewable and Sustainable Energy Reviews 2011;15:4080–106.
[9] Directive 2009/28/EC of the European Parliament and of the Council on the promotion of the use of energy from renewable sources, 2009.
[10] REN21, 2011. Renewables 2011 global status report (Paris: REN21 Secretariat).
[11] Rakopoulos CD, Giakoumis EG. Diesel engine transient operation. London: Springer; 2009.
[12] 〈http://ec.europa.eu/enterprise/sectors/automotive/documents/directives/motor-vehicles/index_en.htm〉, [last accessed 30 August 2012.].
[13] 〈http://www.epa.gov/nvfel/testing〉, [last accessed 30 August 2012.].
[14] Faraco V, Hadar Y. The potential of lignocellulosic ethanol production in the Mediterranean basin. Renewable and Sustainable Energy Reviews 2011;15: 252–66.
[15] Ecklund EE, Bechtold RL, Timbario TJ, McCallum PW State-of-the-art report on the use of alcohols in diesel engines. SAE paper 1984, 840118.
[16] Chotwichien A, Luengnaruemitchai A, Jai-In S. Utilization of palm oil alkyl esters as an additive in ethanol/diesel and butanol–diesel blends. Fuel 2009;88:1618–24.
[17] Rideout G, Kirschenblatt M, Prakash C Emissions from methanol, ethanol, and diesel powered urban transit buses. SAE Paper 1994, 942261.
[18] Wang WG, Clark NN, Lyons DW, Yang RM, Gautam M, Bata RM, et al. Emissions comparisons from alternative fuel buses and diesel buses with a chassis dynamometer testing facility. Environmental Science and Technology 1997;31:3132–7.
[19] Jackson MD, Moyer CB. Alcohol fuels. In Kirk-Othmer, Encyclopedia of Chemical Technology. New York: John Wiley and Sons; 2000.
[20] Meiring P, Allan RS, Hansen AC, Lyne PWL. Tractor performance and durability with ethanol–diesel fuel. Trans ASAE 1983;26:59–62.
[21] Ajav EA, Singh B, Bhattacharya TK. Experimental study of some performance parameters of a constant speed stationary diesel engine using ethanol–diesel blends as fuel. Biomass and Bioenergy 1999;17:357–65.
[22] Chen H, Shuai S, Wang J. Study on combustion characteristics and PM emission of diesel engines using ester–ethanol/diesel blended fuels. Proceedings of the Combustion Institute 2007;31:2981–9.
[23] Rakopoulos CD, Antonopoulos KA, Rakopoulos DC. Experimental heat release analysis and emissions of a HSDI diesel engine fueled with ethanol/diesel fuel blends. Energy 2007;32:1791–808.
[24] Rakopoulos DC, Rakopoulos CD, Kakaras EC, Giakoumis EG. Effects of ethanol/diesel fuel blends on the performance and exhaust emissions of heavy duty DI diesel engine. Energy Conversion and Management 2008;49:3155–62.
[25] Cole RL, Poola, RB, Sekar, R, Schaus, SE, McPartlin P Effects of ethanol additives on diesel particulate and NO_x emissions. SAE Paper 2001, 2001-01-1937.
[26] Kowalewicz A. Eco-diesel engine fuelled with rapeseed oil methyl ester and ethanol. Part 1: Efficiency and emission. Institution of Mechanical Engineers 2005;219(Part D):715–23.
[27] Lapuerta M, Armas O, Herreros JM. Emissions from a diesel–bioethanol blend in an automotive diesel engine. Fuel 2008;87:25–31.
[28] Li D, Zhen H, Xingcai L, Wugao Z, Jianguang Y. Physico-chemical properties of ethanol–diesel blend fuel and its effect on performance and emissions of diesel engines. Renew Energy 2005;30:67–76.
[29] Lapuerta M, Armas O, Garcia-Contreras R. Effects of ethanol on blending stability and diesel engine emissions. Energy Fuels 2009;23:4343–54.
[30] Lapuerta M, Garcia-Contreras R, Campos-Fernandez J, Pilar Dorado M. Stability, lubricity, viscosity, and cold-flow properties of alcohol/diesel blends. Energy Fuels 2010;24:4497–502.
[31] McCormick RL, Parish R. Technical barriers to the use of ethanol in diesel fuel. National Renewable Energy Laboratory Report, NREL/MP-540-32674, 2001.
[32] Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Papagiannakis RG, Kyritsis DC. Experimental-stochastic investigation of the combustion cyclic variability in HSDI diesel engine using ethanol–diesel fuel blends. Fuel 2008;87:1478–91.
[33] Fernando S, Hanna M. Development of a novel biofuel blend using ethanol–biodiesel–diesel microemulsions: EB-diesel. Energy Fuels 2004;18:1695–703.
[34] Yoshimoto Y, Onodera M. Performance of a diesel engine fueled by rapeseed oil blended with oxygenated organic compounds. SAE paper 2002, 2002-01-2854.

[35] Armas O, Martinez-Martinez S, Mata C. Effect of an ethanol–biodiesel–diesel blend on a common rail injection system. Fuel Processing Technology 2011;92:2145–53.
[36] Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Dimaratos AM, Kyritsis DC. Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. Energy Conversion and Management 2010;51: 1989–97.
[37] Rakopoulos DC, Rakopoulos CD, Hountalas DT, Kakaras EC, Giakoumis EG, Papagiannakis RG. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel 2010;89:2781–90.
[38] Yao M, Wang H, Zheng Z, Yue Y. Experimental study of *n*-butanol additive and multi-injection on HD diesel engine performance and emissions. Fuel 2010;89:2191–201.
[39] Lujaji F, Kristof L, Bereczky A, Mbarawa M. Experimental investigation of fuel properties, engine performance, combustion and emissions of blends containing croton oil, butanol, and diesel on a CI engine. Fuel 2011;90:505–10.
[40] Dogan O. The influence of *n*-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions. Fuel 2011;90:2467–72.
[41] Peterson CL, Reece DL. Emission tests with on-road vehicle fueled with methyl and ethyl esters of rapeseed oil. ASAE paper 1994, 946532.
[42] McCormick RL, Ross JD, Graboski MS. Effects of oxygenates on regulated emission from heavy-duty diesel engines. Environmental Science and Technology 1997;31:1144–50.
[43] Spreen K. Evaluation of oxygenated diesel fuels. Final report for Pure Energy Corporation prepared at Southwest Research Institute, San Antonio, TX, 1999.
[44] Ahmed I. Oxygenated diesel: emissions and performance characteristics of ethanol/diesel blends in CI engines. SAE paper 2001, 2001-01-2475.
[45] Corkwell KC, Jackson MM, Daly DT Review of exhaust emissions of compression ignition engines operating on E diesel fuel blends. SAE paper 2003, 2003-01-3283.
[46] Frank PB, Tang S, Lanni T, Rideout G et al. A study of the effects of fuel type and emission control systems on regulated gaseous emissions from heavy-duty diesel engines. SAE paper 2004, 2004-01-1085.
[47] Fanick ER Fuel and fuel additive registration testing of ethanol/diesel blend for O_2 diesel, Inc. National Renewable Energy Laboratory Report, NREL/SR-540-35334, 2004.
[48] Merritt PM, Ulmet V, McCormick RL, Mitchell WE, Baumgard KJ Regulated and unregulated exhaust emissions comparison for three Tier II non-road diesel engines operating on ethanol/diesel blends. SAE paper 2005, 2005-01-2193.
[49] Armas O, Cardenas MD, Mata C Smoke opacity and NO_x emissions from a bioethanol/diesel blend during engine transient operation. SAE paper 2007, 2007-24-0131.
[50] Tang S, Frank BP, Lanni T, Rideout G, Meyer N, Beregszaszy C. Unregulated emissions from a heavy-duty diesel engine with various fuels and emission controls. Environmental Science and Technology 2007;41:5037–43.
[51] Glancey JL, Chirnside A, Hummel J, Nobles S, Chanpimol S, Raval A Measurement of transient smoke emissions characteristics from e-diesel and soy-diesel fuel blends in two commercial engines. 2007 ASAE Annual Meeting 076093.
[52] Miers SA, Carlson RW, McConnell SS, Ng HK, Wallner T, Esper JL Drive cycle analysis of butanol/diesel blends in a light-duty vehicle. SAE paper 2008, 2008-01-2381.
[53] Armas O, Lapuerta M, Mata C, Perez D. Online emissions from a vibrating roller using an ethanol/diesel blend during a railway construction. Energy Fuels 2009;23:2989–96.
[54] Löfvenberg U. Short report from emission test using low blend of ethanol derivative in diesel fuel. TREN/05/FP6EN/S07.53807/019854, 2009.
[55] Rakopoulos CD, Dimaratos AM, Giakoumis EG, Rakopoulos DC. Investigating the emissions during acceleration of a turbocharged diesel engine operating with biodiesel or *n*-butanol diesel fuel blends. Energy 2010;35:5173–84.
[56] Cheenkachorn K, Fungtammasan B. An Investigation of diesel–ethanol–biodiesel blends for diesel engine: Part 2 Emission and engine performance of a light-duty truck. Energy Sources 2010;32(Part A):894–900.
[57] Rakopoulos CD, Dimaratos AM, Giakoumis EG, Rakopoulos DC. Study of turbocharged diesel engine operation, pollutant emissions and combustion noise radiation during starting with biodiesel or *n*-butanol diesel fuel blends. Applied Energy 2011;88:3905–16.
[58] Randazzo ML, Sodre JR. Exhaust emissions from a diesel powered vehicle fuelled by soybean biodiesel blends (B3–B20) with ethanol as an additive (B20E2–B20E5). Fuel 2011;90:98–103.
[59] Kozak MJ Exhaust emissions from a diesel passenger car fuelled with a diesel fuel–butanol blend. SAE Paper 2011, 2011-28-0017.
[60] Magand S, Pidol L, Chaudoye F, Sinoquet D, Wahl F, Castagne M, et al. Use of ethanol/diesel blend and advanced calibration methods to satisfy Euro 5 emission standards without DPF. Oil & Gas Science and Technology 2011;66 85–75.
[61] Hulwan DB, Joshi SV. Performance, emission and combustion characteristic of a multicylinder DI diesel engine running on diesel–ethanol–biodiesel blends of high ethanol content. Applied Energy 2011;88:5042–55.
[62] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Combustion noise radiation during acceleration of a turbocharged diesel engine operating with biodiesel or *n*-butanol diesel fuel blends. Institution of Mechanical Engineers 2012;226(Part D):971–86.
[63] Ballesteros R, Hernandez JJ, Guillen-Flores J. Carbonyls speciation in a typical European automotive diesel engine using bioethanol/butanol–diesel blends. Fuel 2012;95:136–45.
[64] Armas O, Garcia-Contreras R, Ramos A. Pollutant emissions from engine starting with ethanol and butanol diesel blends. Fuel Processing Technology 2012;100:63–72.
[65] Tree DR, Svensson KI. Soot processes in compression ignition engines. Progress in Energy and Combustion Science 2007;33:272–309.
[66] Randazzo ML, Sodre JR. Cold start and fuel consumption of a vehicle fuelled with blends of diesel oil–soybean biodiesel–ethanol. Fuel 2011;90:3291–303.
[67] Sharp CA, Howell SA, Jobe J The effect of biodiesel fuels on transient emissions from modern diesel engines—Part I: Regulated emissions and performance. SAE paper 2000, 2000-01-1967.
[68] Shudo T, Nakajima T, Hiraga K. Simultaneous reduction in cloud point, smoke, and NO_x emissions by blending bioethanol into biodiesel fuels and exhaust gas recirculation. International Journal of Engine Research 2009;10: 15–26.
[69] Botero ML, Huang Y, Zhu DL, Molina A, Law CK. Synergistic combustion of droplets of ethanol, diesel and biodiesel mixtures. Fuel 2012;94:342–7.
[70] Law CK. Combustion physics. Cambridge: Cambridge University Press; 2006.
[71] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends. Progress in Energy and Combustion Science 2012;38: 691–715.
[72] Bannister CD, Hawley JG, Ali HM, Chuck CJ, Price P, et al. The impact of biodiesel blend ratio on vehicle performance and emissions. Institution of Mechanical Engineers 2010;224(Part D):405–21.
[73] Muncrief RL, Rooks CW, Cruz M, Harold MP. Combining biodiesel and exhaust gas recirculation for reduction in NO_x and particulate emissions. Energy Fuels 2008;22:1285–96.
[74] Guarieiro LLN, de Souza AF, Torres EA. Emission profile of 18 carbonyl compounds, CO, CO2, and NO_x emitted by a diesel engine fuelled with diesel and ternary blends containing diesel, ethanol and biodiesel or vegetable oils. Atmospheric Environment 2009;43:2754–61.
[75] Hurley MD, Wallington TJ, Laursen L, Javadi MS, Nielsen OJ, Yamanaka T, et al. Atmospheric chemistry of *n*-butanol: kinetics, mechanisms, and products of Cl atom and OH radical initiated oxidation in the presence and absence of NO_x. Journal of Physical Chemistry A 2009;113:7011–20.
[76] Miyamoto N, Ogawa H, Nurun N, Obata K, Arima T Smokeless, low NO_x, high thermal efficiency, and low noise diesel combustion with oxygenated agents as main fuel. SAE Paper 1998, 980506.
[77] Donahue RJ, Foster DE Effects of oxygen enhancement on the emissions from a DI diesel via manipulation of fuels and combustion chamber gas composition. SAE Paper 2000, 2000-01-0512.
[78] Giakoumis EG. A statistical investigation of biodiesel effects on regulated exhaust emissions during transient cycles. Applied Energy 2012;98:273–91.
[79] Szybist JP, Song J, Alam M, Boehman A. Biodiesel combustion, emissions and emission control. Fuel Processing Technology 2007;88:679–91.
[80] Lapuerta M, Armas O, Rodriguez-Fernandez J. Effect of biodiesel fuels on diesel engine emissions. Progress in Energy and Combustion Science 2008;34: 198–223.
[81] Park SH, Yun IM, Lee CS. Influence of two-stage injection and exhaust gas recirculation on the emissions reduction in an ethanol-blended diesel-fueled four cylinder diesel engine. Fuel Processing Technology 2010;91:1753–60.
[82] Lilly LRC. Diesel engine reference book. London: Butterworths; 1984.
[83] Russell MF, Haworth R. Combustion noise from high speed direct injection diesel engines. SAE paper 1985, 850973.
[84] Zurita-Villaroel G, Pettersson E, Angren A Multivariate analysis of engine noise and exhaust emissions from an ethanol fuelled diesel engine. SAE Paper 1997, 971871.
[85] Kumar C, Athawe M, Aghav YV, Gagendar Babu MK, Das LM Multivariate analysis of engine noise and exhaust emissions from an ethanol fuelled diesel engine. SAE Paper 2007, 2007-01-0626.
[86] Cong S, Garner CP, McTaggart-Cowan GP. The effects of exhaust back pressure on conventional and low-temperature diesel combustion. Institution of Mechanical Engineers 2011;225(Part D):222–35.
[87] Valentino G, Corcione FE, Iannuzzi SE, Serra S. Experimental study on performance and emissions of a high speed diesel engine fuelled with *n*-butanol diesel blends under premixed low temperature combustion. Fuel 2012;92:295–307.
[88] Pidol L, Lecointe B, Starck L, Jeuland L. Ethanol–biodiesel–diesel fuel blends: performances and emissions in conventional diesel and advanced low temperature combustions. Fuel 2012;93:329–38.